

REPORT #5-  
6-1-64 - 1-31-65

ON

THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF  
HEAT-RESISTANT POLYMERS

TO

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON, D.C.

PERFORMED

UNDER

NSG-399  
NASA GRANT No 339

APRIL, 1965

N 65-85619  
(ACCESSION NUMBER)  
103  
(PAGES)  
(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA

PROGRESS REPORT NUMBER 5

ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF  
HEAT-RESISTANT POLYMERS

PERFORMED

UNDER

NASA GRANT NsG339

BY

G. F. D'ALELIO

PRINCIPAL INVESTIGATOR

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA

APRIL 15, 1965

## FOREWORD

This report is a summary report of the researches performed under NASA Grant Nsg339 for the period 1 June 1964 to 31 January 1965 on the synthesis of heat-resistant polymers. The technical aspect of this grant is administered by Mr. Bernard Achhammer, Office of Advanced Research and Technology, NASA Headquarters, Washington, D. C.

The research under this grant is being conducted in the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana under the technical direction of Professor G. F. D'Alelio, principal investigator.

This report covers studies performed by G. F. D'Alelio, T. Kurosaki, and J. Crivello.

Date April 15, 1965

Signed G. F. D'Alelio  
G.F. D'Alelio  
Principal Investigator

## TABLE OF CONTENTS

I.	Introduction-----	1
II.	Synthesis of New Monomers and Related Azomethines-----	2
	A. Simple Schiff Bases-----	2
	B. Monomeric Schiff Bases-----	3
III.	Non-Polymeric Prototype Schiff Base Reactions-----	5
	A. Experimental-----	6
	B. Discussion-----	8
IV.	Polymerization Reactions-----	9
	A. Polymerizations of Diamines and Dialdehydes-----	9
	1. Experimental-----	9
	2. Discussion-----	11
	B. Amine Exchange Polymerizations-----	12
	1. Experimental-----	12
	2. Discussion-----	16
	C. Carbonyl Exchange Polymerizations-----	17
	1. Experimental-----	18
	2. Discussion-----	25
	D. Bis-Schiff Base Exchange Polymerizations-----	26
	1. Experimental-----	27
	2. Discussion-----	34
	E. Thermal Stability of Monomeric Schiff Bases and Mixtures with Monoacetal-----	35
	1. Experimental-----	36
	2. Discussion-----	37

F. Reactions of Xylylidenetetraethyl Ether,	
Dibenzylidene-p-phenylene Diamine in Benzal-	
aniline at Temperatures in Excess of 300°C-----	37
1. Polymerization at 300°C-----	37
a. Experimental-----	38
b. Discussion-----	40
2. Post-Heating of Polymerization Products-----	40
a. Experimental-----	41
b. Discussion-----	43
3. Identification of Distillates due to Post-Heating-----	43
4. IR Spectra of Polymers Before and After Heating-----	46
5. Solvent Extraction of Polymers-----	46
a. Experimental-----	51
b. Discussion-----	51
6. General Discussion-----	52
G. Polymerization of Xylylidenetetraethyl Ether with	
m-Phenylenediamine in Benzalaniline-----	54
1. Experimental-----	55
2. Discussion-----	58
H. Polymerization of Xylylidenetetraethyl Ether	
with Dibenzylidene-m-phenylenediamine in	
Benzalaniline-----	58
1. Experimental-----	59
2. Discussion-----	60
I. Polymerization of Phenylenediamines or	
Dibenzylidene-phenylenediamines in an Excess	
of Xylylidenetetraethyl Ether-----	61

1. Experimental-----	62
2. Discussion-----	64
J. Polymerization of Xylylidenetetra-n-butyl Ether	
with p-Phenylenediamines or its Derivatives-----	65
1. Polymerizations of Xylylidenetetra-n-butyl	
Ether with p-Phenylenediamine-----	66
a. Experimental-----	66
b. Discussion-----	68
2. Polymerization of Xylylidenetetra-n-butyl Ether	
with Dibenzylidene-p-phenylenediamine-----	69
a. Experimental-----	69
b. Discussion-----	70
3. Polymerization of Xylylidenetetra-n-butyl Ether	
with Di-N-acyl-p-phenylenediamine-----	70
a. Experimental-----	70
b. Discussion-----	71
K. Preliminary Evaluation of a Mixed Acetal and	
its Polymerization with a Diamine-----	71
1. Synthesis of a Mixed Acetal-----	71
2. Polymerization of a Mixed Acetal with	
p-Phenylenediamine-----	72
a. Experimental-----	72
b. Discussion-----	73
L. Polymerization of Xylylidenetetraalkyl Ether with	
Mono-benzalphenylenediamine-----	73
1. Experimental-----	75
2. Discussion-----	78

V. Post Reactions of Polymers-----	79
A. Post Reactions Leading to an Increase in the Degree of Polymerization-----	79
1. Experimental-----	79
2. Discussion-----	81
B. Attempts to Determine the Solubility of Certain Polymers-----	82
1. Experimental-----	82
2. Discussion-----	82
VI. Mechanistic Considerations and Attempts to Isolate Intermediates-----	84
A. Experimental-----	84
B. Discussion-----	87
VII. Summary and Conclusion-----	89
VIII. Future Studies-----	92
IX. Acknowledgment-----	94
X. Glossary-----	95
XI. Bibliography-----	96

## I. Introduction.

In a previous report,<sup>1</sup> a number of reaction systems for the synthesis of conjugated polymeric Schiff bases were selected for continued study. Such studies were necessary to complete the preliminary investigations to obtain more data on which the final selections of the polymerization systems would be made. The investigations included the syntheses of some new monomers, non-polymeric prototype Schiff base reactions, a large number of selected polymerizations, post-reactions of conjugated polymers and some attempts to determine reaction mechanisms.

The experimental data in this report complete the preliminary studies and establish the basis for the researches to be performed during the period of February 1965 to January 1966.



## II. Synthesis of New Monomers and Related Azomethines.

A number of Schiff bases were synthesized during the course of this research as they were needed. These compounds were prepared by the simple condensation of the appropriate amines and aldehydes according to the method reported by Schiff.<sup>2</sup> In those cases, in which the reported yields were satisfactory, the procedure described<sup>3</sup> in Organic Synthesis Collective Volume I was used. In the cases where the yields were described as poor or not listed, an azeotrope method was used, whereby water is removed as a by-product of the reaction and collected in a Dean-Stark trap by virtue of its formation of an azeotrope with benzene. This method, previously described<sup>1</sup> in a NASA report, has been applied to the synthesis of a large number of Schiff bases, and has been found to be successful in all cases giving high yields and pure products.

### A. Simple Schiff Bases.

Table 1 gives a number of simple Schiff bases prepared by the condensation of an aromatic amine with an aromatic aldehyde. Some of the compounds included in the previous report<sup>1</sup> have been included in this table for completeness.

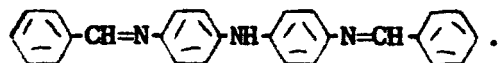
Table 1

Data on Some Schiff Bases

Exper. No.	Compound	Ref.	M.P. °C	Ref. M.P. °C	Crude Yield %
DA-29-142	$p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_5$	4	71	72	86.5
DA-29-143	$p\text{-O}_2\text{N-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_5$	5	93	93	93.3
DA-29-144	$m\text{-O}_2\text{N-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_5$	6	66	66	91.6
DA-29-161	$p\text{-Br-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_5$	-	65	--	Quant.
DA-29-109	$p\text{-HO-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_5$	7	199	190-200	Quant.
DA-29-171	$m\text{-O}_2\text{N-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_5$	8	73	73	Quant.

### B. Monomeric Schiff Bases.

For use as reagents for polymerizations to be performed later, a number of bis-Schiff bases having potential functionalities of two were synthesized. A special procedure was devised for the preparation of the bis-Schiff base,



Since the triamine 4,4'-diaminodiphenylamine could be obtained only as the monosulfate salt, the azeotropic method was not used. It was decided that the liberation of the free amine and synthesis therefrom of the bis-Schiff base could be done in one reaction vessel. The amine salt was first dissolved in water, benzene added, and the free amine was liberated by the action of an equivalent quantity of sodium hydroxide. The free amine, being insoluble in water, then passed into a benzene layer in the reaction vessel containing two equivalents of benzaldehyde. Reaction occurred in the benzene layer giving the bis-Schiff base. The water layer was separated by means of a separatory funnel; the desired product was isolated from the benzene layer. The low yield of pure product (29.1%) was due to the impurities in the starting materials (the triamine was Aldrich technical grade) and various losses during the many recrystallizations.

A separate procedure was also employed for the attempted synthesis of the diamino compound,  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$ , from p-phenylenediamine (PPDA) and terephthalaldehyde (TA). To avoid polymerization of the starting materials, 0.15 mole of PPDA was dissolved in a large volume of ethanol (~500 ml.) and heated to boiling. Next, 0.6 mole of TA, dissolved in 120 ml. ethanol, was added to the reaction dropwise over the course of one hour.

The product obtained from this reaction was a yellow amorphous powder having no melting point and was only slightly soluble in acetone or ethanol.

It was concluded that a polymer had been formed rather than the desired diamino product.

A number of the monomeric bis-Schiff bases were prepared by the azeotropic method as well defined yellow crystalline compounds. The monomeric bis-Schiff bases prepared during this period are summarized in Table 2.

Table 2

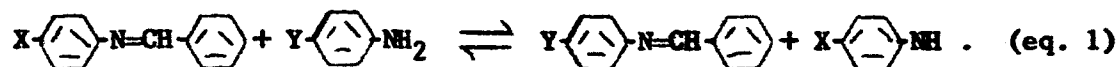
Data on Some Monomeric Schiff Bases

Exper. No.	Compound	Ref.	M.P. °C	Ref. M.P. °C	Crude Yield %
DA-29-176	$\text{C}_6\text{H}_5\text{-CH=N-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_5$	9	130	125-126	Quant.
DA-29-178	$\text{C}_6\text{H}_5\text{-CH=N-(CH}_2\text{)}_4\text{-N=CH-C}_6\text{H}_5$	--	26-27	-----	Quant.
DA-29-181	$\text{C}_6\text{H}_5\text{-CH=N-(CH}_2\text{)}_6\text{-N=CH-C}_6\text{H}_5$	10 11	25	28-32	Quant.
DA-29-184	$\text{C}_6\text{H}_5\text{-CH=N-C}_6\text{H}_4\text{-O-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_5$	--	182-183	-----	Quant.
DA-29-188	$\text{C}_6\text{H}_5\text{-CH=N-C}_6\text{H}_4\text{-NH-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_5$	--	183-186	-----	29.1 (pure)
DA-29-201	$\text{H}_2\text{N-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-NH}_2$	--	polymer	-----	-----

It is noted that all the monomers in Table 2 have either total or partial interruption of conjugation by means of a heteroatom or saturated aliphatic moiety. By utilizing these monomers in either the bis-Schiff base exchange or the carbonyl exchange reactions, it will be possible to obtain polymers with various degrees of conjugation. The polymers whose conjugation is interrupted by oxygen or nitrogen are expected to retain a large measure of their conjugation,<sup>12</sup> whereas those interrupted with aliphatic groups would be expected to retain little or less conjugation. By comparison of the heat stabilities of these polymers with polymers possessing uninterrupted conjugation, an evaluation of the contribution of conjugation to heat stability can be made.

### III. Non-Polymeric Prototype Schiff Base Reactions.

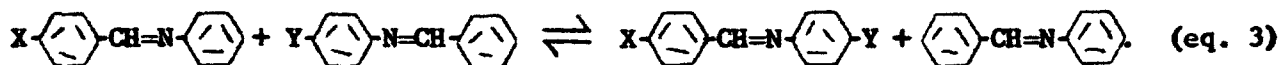
In a previous report<sup>1</sup> three exchange reactions of Schiff bases were discussed. The first of these is an amine exchange reaction whereby the amino residue of a Schiff base can be replaced in a reaction with another amine, for example:



The second is an exchange of the carbonyl moiety of a Schiff base by reaction with an aldehyde or ketone, thus:



The third is the bis-exchange reaction in which two different Schiff bases participate by exchanging amine and carbonyl moieties, thus producing two new Schiff base compounds, as shown in equation 3:

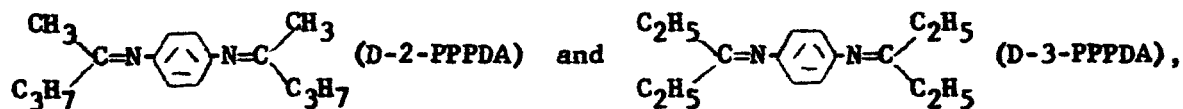


The primary factors involved in these exchange reactions are 1) the reactivity of the reagents and 2) the volatility of the product or by-product.<sup>12</sup> In exchange reactions, the products formed from the reaction must be more stable than the starting materials for the reaction to occur, and the reactivity of the starting materials must be high. To achieve a high degree of conversion in the exchange reactions, which are equilibrium processes, it has been found necessary to remove one or both of the products to shift the equilibrium. The research contained in this and in the previous report<sup>1</sup> confirms the results of Reddelein, that quantitative yields of products may be obtained by distilling out one of the products of the reaction.

A number of monomers and related Schiff base compounds were prepared and non-polymeric prototypes of the three exchange reactions were studied. Having established first that the reactions took place, and second, the conditions under which the exchanges took place readily, suitable monomers were poly-

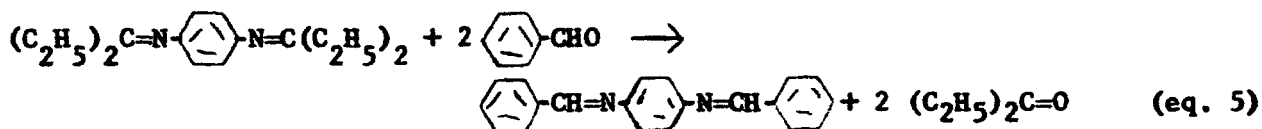
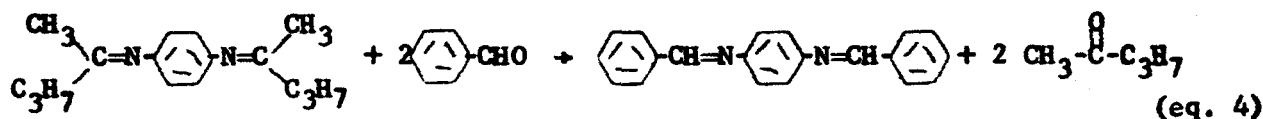
merized, yielding black conjugated polymeric Schiff bases.

In a previous report the synthesis of two new monomers,



were described.<sup>1</sup> These compounds were prepared for the purpose of obtaining monomers with greater reactivities in Schiff base exchange reactions than dibenzylidene-p-phenylenediamine (DBPPDA). Preparatory to using these new monomers in polymerization reactions, prototype reactions were run to determine the relative reactivities of the new monomers.

Since the reactivity of aldehydes in the formation of Schiff bases is greater than ketones, it would seem reasonable that an appropriate aldehyde should be able to replace a ketone from its Schiff base. Thus, in the reaction between a diketonanil and benzaldehyde, the products expected would be DBPPDA and the displaced ketone, thus:



#### A. Experimental.

##### 1. (DA-29-103) Reaction of Benzaldehyde and Di(2-pentylidene)-p-phenylenediamine.

In a 50 ml. round-bottomed flask were placed 0.02 mole of the diketonanil and 0.04 mole of freshly distilled benzaldehyde. After a short time, a yellow solid began to precipitate from the reaction mixture and to collect at the bottom of the flask. The flask was now modified for distillation under nitrogen by the addition of a suitable distillation head, condenser, receiver, and

nitrogen inlet. Distillation was begun at 140°C and continued at this temperature for one hour. Some small amount of liquid was collected in the receiver during this time. Next, the temperature was raised to 200°C over a period of two hours, and additional distillate was collected. The distillate was examined and found to consist of two layers. Samples were subjected to infrared analysis and found to be water and 2-pentanone. The amounts of each of the two compounds collected were 2.2 g. and 1.6 g. respectively. The residue was found to be a dark-yellow viscous liquid which did not crystallize upon cooling. Attempted recrystallizations from hexane and ethanol did not yield a crystalline material.

## 2. (DA-29-106) Modification of DA-29-103 at Lower Temperatures.

Di-(2-pentylidene)-p-phenylenediamine, 0.01 mole, and 0.02 mole of benzaldehyde were mixed together in a small beaker and allowed to stand at room temperature for one hour. A yellow solid rapidly separated from the mixture and the crystals were collected by filtration. The compound was then recrystallized from 95% ethanol containing activated charcoal. Yellow, well-defined crystals were obtained which melted at 140°C, corresponding to the melting point of DBPPDA prepared by a different route.

## 3. (DA-29-145) Reaction of Benzaldehyde and Di-(3-pentylidene)-p-phenylenediamine.

Benzaldehyde 2.12 g. (0.02 mole) and 2.44 g. (0.01 mole) di-(3-pentylidene)-p-phenylenediamine were mixed together in a 50-ml. beaker. Within a few minutes the color of the reaction mixture had deepened from yellow to light orange. As the mixture was stirred, an evolution of heat was noted, together with the odor of diethylketone. After ten minutes the reaction mixture became solid. The beaker was placed on a steam bath and heated for one and one-half hours, and the resulting product was then dried in

a vacuum desiccator. Recrystallization from 95% ethanol gave a yellow crystalline product which melted at 140°C. This melting point is identical to that of DEPPDA. The yield of product after recrystallization was 47.2%.

#### B. Discussion.

Both prototype reactions studied indicate that the new ketanil monomers have a high reactivity. The reactions occur smoothly at room temperature or slightly above, to yield the desired products. These reactions indicate clearly the superior reactivity of selected aromatic aldehydes over the aliphatic ketones in the carbonyl Schiff base exchange reactions. The reactions also demonstrate the great facility and generality of the carbonyl exchange reaction. On the basis of these prototype reactions one may expect these compounds to be especially effective as monomers in polymerizations.

#### IV. Polymerization Reactions.

In this phase of research, further studies were conducted along the lines of research described and carried out in the previous report.<sup>1</sup> In some cases, however, significant changes were made in the experimental techniques used in the polymerization reactions. New monomers were also synthesized and introduced into the polymerizations, thereby increasing the number of routes to the preparation of aromatic conjugated Schiff base polymers.

##### A. Polymerizations of Diamines and Dialdehydes.

Some Schiff base polymers have been prepared previously by this method, that is, by the condensation of a suitable diamine and dialdehyde with the elimination of water:<sup>13</sup>



Polymers obtained by this method are low molecular weight, yellow, insoluble, infusible solids. Attempts were made to improve the reaction in order to attain higher molecular weights. It was decided that the main cause of low molecular weight polymers in this reaction was due to early precipitation of the polymer from the reaction system. A non-homogeneous reaction system is thus obtained which effectively inhibits further polymerization. It was believed that if a suitable solvent could be found, the reaction could be propagated to higher molecular weights. Benzalaniline and dimethylformamide were selected and evaluated as solvents for the condensation reactions.

##### 1. Experimental.

###### a. (DA-29-129) Condensation-Melt Polymerization Using Benzalaniline. (Repeat of DA-29-67)

Ten grams of benzalaniline (BA) and 1.08 g. (0.01 mole) PPDA were mixed thoroughly in a 50-ml. round-bottomed microflask. The microflask was heated by means of a metal bath to 120°C and then 1.34 g. (0.01 mole) TA were added



to this reaction mixture. The flask was then fitted with a distilling head, nitrogen inlet, condenser, and receiver. Heating was continued according to the schedule of Table 3.

Table 3

Time (hours)	Temp. °C	Pressure
2	120-200	atm
5	220	atm
10	260	atm
10	290	atm
10	290	140 mm

Water and BA were recovered in the receiver and the reaction flask yielded a dull brown material which was non-fusible. Yield of polymer obtained was 107.8% of the theoretical.

b. (DA-29-131) Further Modification of DA-29-129 and DA-29-67.

The same quantities of reagents and the same mode of addition were used in this experiment as were used previously. The times and temperatures used in the polymerization step, however, were modified. The schedule used during the reaction is given in Table 4.

Table 4

Time (hours)	Temp. °C	Pressure
4	120-200	atm
12	240	atm
10	240	atm
10	240	140.0 mm
10	320	0.5 mm

When the reaction was terminated, a brown-black polymer was obtained which was

porous and infusible. Due to mechanical losses only 0.95 g. of polymer was recovered in the reaction.

c. (DA-29-195) Reaction in DMF.

PPDA 1.08 g. (0.01 mole) was added to a small round-bottomed flask containing 50 ml. dimethylformamide and 1.34 g. (0.01 mole) TA. Immediately upon adding the amine, the solution became yellow-orange. Gradually the color deepened into dark orange. The flask was fitted with a reflux condenser and the reaction mixture refluxed for two and one-half hours. Five minutes after the heating began a yellow precipitate formed in the reaction mixture. The amount of precipitate increased during the period of reflux, accompanied by a decrease in the orange color of the solution. Then, after two and one-half hours, most of the dimethylformamide was removed by distillation. During the distillation, dimethylamine, which was assumed to have been produced by amide-exchange during the reaction, was detected as a non-condensing gas. When the major portion (about 80%) of the DMF was collected, the polymer was isolated by filtration and dried in a drying oven for four hours; 2.42 g. (117% yield) of an orange polymer was obtained.

To the DMF-water filtrate there was added 20 ml. benzene and the mixture was azeotroped. The water which azeotroped with the benzene was measured and found to be 0.301 g. or 83.6% theory.

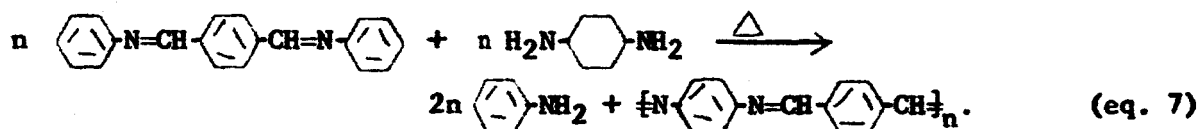
2. Discussion.

It has been shown by the above experiments that even the condensation reaction which previously gave only yellow low-molecular-weight polymers may be carried to higher molecular weights by the use of an appropriate solvent. Common solvents, such as benzene, ethanol, and DMF fail to solvate the growing chain to any significant extent. Thus, premature precipitation of the polymer occurs, resulting in effective termination of polymerization at the limit of

solubility in the solvent. The resulting polymers themselves are brittle, porous, infusible materials which are also insoluble in common solvents. Benzalaniline, however, which is structurally like the polymer itself, appears to be an effective solvent for the reaction. Polymers obtained in those cases where BA was used are usually found to have incorporated some of this substance, as indicated by yields in excess of 100%.

### B. Amine Exchange Polymerizations.

As described earlier,<sup>1</sup> it has been found possible to replace the amino moiety of a Schiff base with a different amine in a reaction we have termed an amine Schiff base exchange reaction. If a difunctional amine reacts with a bis-Schiff base of a dialdehyde and a monoamine, polymers are obtained, as shown in equation 7:



The polymers obtained in this reaction are identical with those produced by the condensation reaction except for the end groups. Amine exchange polymerizations were carried out both by melt-solution techniques, in which the monomers are melted together in the presence of BA, and by straight solution techniques.

## 1. Experimental.

### a. Solution Polymerizations.

Benzalaniline was used in these systems after having found that the simple melt polymerization of PPDA and p-xylylidinedianil (PXDA) resulted in the formation of low molecular weight yellow-brown oligomers. To increase the molecular weight, BA was added in these polymerizations as a solvent to provide a homogeneous medium in which the polymer could propagate.

i. (DA-29-135) Reaction of PXDA with PPDA in the Presence of Benzalaniline. (Repeat of DA-29-63 and DA-29-65)

Using the same polymerization apparatus employed in the above condensation polymerizations, 2.84 g. (0.01 mole) PXDA, 1.08 g. (0.01 mole) PPDA and 3 g. BA were mixed together. After placing the reagents in the polymerization apparatus, the mixture was heated, using a metal bath under the conditions given in Table 5.

Table 5

Time (hours)	Temp. °C	Pressure
4	160	atm
15	250	atm
10	310	atm
15	330	140 mm
10	350	0.1 mm

As the polymerization was continued, the reaction mixture underwent the usual shift in color from yellow to red to brown to black. The polymer, at the end of the reaction time, was a black, very brittle, shiny polymer, which melted and foamed considerably when held on a spatula in the flame of a bunsen burner. The weight of polymer obtained was 3.79 g., which exceeded 2.06 g. calculated for the theoretical yield. The yield of product obtained indicates that all of the BA and by-products of the reaction had not been completely removed.

ii. (DA-29-139) Modification of DA-29-135.

Experiment DA-29-135 was repeated using the same quantities of reagents and apparatus, but with the modification shown in Table 6. A coal black polymer, 2.44 g., was obtained having both dull and shiny portions. This polymer was infusible even at bunsen flame temperatures, and the amount of by-product material retained in the polymer was considerably less than before.

Table 6

Time (hours)	Temp. °C	Pressure
4	160	atm
10	260	atm
10	340	atm
12	340	140.0 mm
10	340	0.3 mm

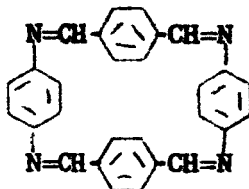
#### b. Other Solution Polymerizations.

Several of the amine exchange polymerizations were performed in the presence of solvents other than benzalaniline. Benzene and tetralin were used as examples of high- and low-boiling solvents. These experiments were carried out in order to determine whether or not the polymerization would proceed at low temperatures, and if the polymerization did occur, would the polymer obtained by this method be any different than the polymers obtained by the melt, or melt-solution methods. Accordingly, the following experiments were performed.

##### i. (DA-29-167) Reaction of PPDA and PXDA in Boiling Benzene.

A mixture of PXDA 2.84 g. (0.01 mole) and 1.08 g. (0.01 mole) PPDA were dissolved in 200 ml. benzene. Then, the reaction mixture was refluxed for about one hour. No reaction appeared to be taking place, so 0.002 g. p-toluenesulfonic acid was added as a catalyst. Within a short time, a yellow flocculent precipitate was observed in the reaction mixture. After refluxing for twelve hours, the reaction was discontinued and the yellow low molecular weight oligomer was filtered off; 2.31 g. of product (112% theoretical) was obtained in this manner. The yellow filtrate from the reaction was refluxed for another twelve hours and upon cooling the solution, two products were

obtained. The first was a greenish, amorphous solid which appeared on the basis of infrared spectra, to be  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$ . The second material was a well-defined clear orange crystalline substance which, upon standing, became opaque. The infrared spectrum showed strong peaks in the carbon-nitrogen double bond and in the phenylene region. Peaks attributable to mono-substituted phenyl groups were absent. On the basis of this information, the following structure is considered possible for the second compound:



ii. (DA-29-170) Modification of DA-29-167 Using a More Dilute System.

Five millimoles each of the reagents in 300 ml. benzene were refluxed without a catalyst for twelve hours. A yellow amorphous powdery substance, weighing 0.95 g., was obtained. This material had a large number of peaks identifiable as Schiff base peaks. The filtrate was isolated and 2 milligrams of p-toluenesulfonic acid was added to it as a catalyst. Immediately upon adding the catalyst, the solution became cloudy and a tan material precipitated. This solution was now refluxed for another twelve hours, and at the end of that time 0.21 g. of a tan precipitate was collected by filtration. Comparison by infrared spectroscopy of this material with the yellow substance obtained before by infrared showed that both spectra contained the same peaks. It was concluded that the tan compound had a higher molecular weight than the yellow compound.

When both of the compounds were heated, they melted, slowly changed color, and became black.

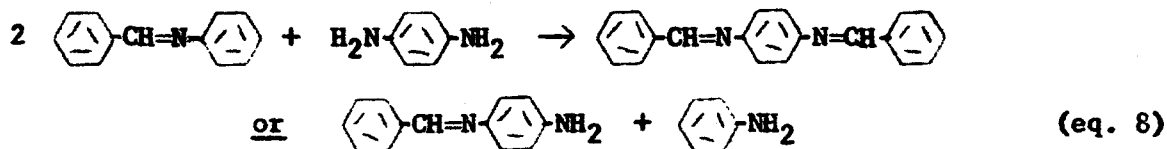
ii. (DA-29-173) Attempted Further Polymerization of DA-29-167 in Tetralin.

One gram of the yellow polymer obtained in experiment DA-29-167 was placed in a 150 ml. of tetralin and the mixture was heated to reflux. After twenty-seven hours of reflux the boiling tetralin solution became homogeneous, all of the yellow polymer went into solution. When the reaction was cooled, a yellow substance precipitated which appeared no different than the starting material. Upon drying and weighing 0.97 g. polymer was recovered. The filtrate, when examined, exhibited fluorescence.

2. Discussion.

It has been shown that benzalaniline, when used in an amine exchange melt-solution polymerization, enables the reaction to proceed to a higher degree of polymerization than when it is absent. The function of BA appears to be that of a solvent which, by solvating the growing polymer chains, keeps the polymer in solution, thus enabling them to propagate to higher molecular weights. It is recognized<sup>1</sup> also, the effect of BA may not be entirely due to its solvent properties. In such systems as the Schiff base exchange reactions, BA may be a reactant as well as acting as a solvent.

A reaction may take place between BA and one of the monomers before or during the actual polymerization. For example, in the amine exchange, PPDA may react with BA in a separate amine exchange to give dibenzylidene-p-phenylenediamine, or mono benzyldene-p-phenylenediamine, thus:



Reaction of one or both of the products of this reaction with PXDA may lead to the polymer. Thus, the final polymer would be expected to be terminated or telomerized by phenyl groups derived from BA.

Solution polymerizations of PPDA and PXDA yield, as expected, low molecular weight oligomers. Solubility seems to be the factor that exerts a major control on molecular weight of the polymer in solution polymerizations. The extent of polymerization is effectively restricted by the solubility of the polymer in the solvent. The expected increase in molecular weight with increased temperature was not observed in the case of high boiling tetralin.

The oligomers obtained by solution polymerization differed significantly from low molecular weight polymers produced by previous methods. When these polymers were warmed slightly, they melted, readily changing color, and could be carried to a dark, high molecular weight product by continued heating at higher temperatures. Yellow oligomers obtained by other methods did not melt or react significantly when heated and the products obtained were not black but yellow. Solution polymerizations, therefore, yield low molecular weight polymers with reactive end groups which can further react to give higher molecular weight products.

### C. Carbonyl Exchange Polymerizations.

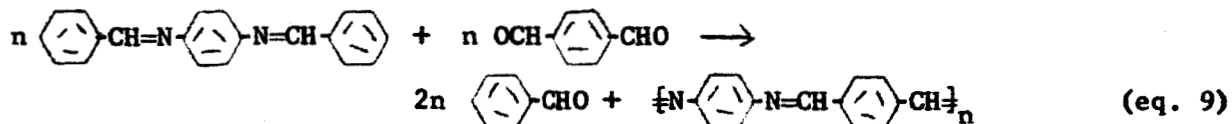
Prototype studies conducted on the exchange reaction between aldehydes and Schiff bases indicated that this reaction occurs with about the same facility as the amine exchange reaction. Several melt polymerizations were performed and reported<sup>1</sup> previously. These polymerizations were repeated again under different conditions to find improved conditions for the preparation of polymers by this exchange method. The two new monomers, di-(2-pentylidene)-p-phenylenediamine (D-2-PPFDA) and di-(3-pentylidene)-p-phenylenediamine (D-3-PPFDA) were also used in carbonyl exchange polymerizations, thus extending the scope of the reaction. As in the amine exchange reaction, melt-solution and solution polymerizations were also investigated.



## 1. Experimental.

### a. Melt Polymerizations.

The reaction between TA and DBPPDA is given in equation 9,



Experiment DA-29-40, which was reported<sup>1</sup> previously, was repeated to determine whether the reaction could be improved by varying the conditions of temperature, pressure and time.

#### i. (DA-29-123) Reaction of TA and DBPPDA. (Repeat of DA-29-40)

The following quantities of reagents were placed in a 50 ml. round-bottomed flask: 1.34 g. (0.01 mole) TA and 2.84 g. (0.01 mole) DBPPDA. Using the usual polymerization apparatus consisting of reaction flask, distillation head, nitrogen inlet, condenser, and receiver, the reaction mixture was heated by means of a metal bath. The conditions used during the polymerization are given in Table 7.

Table 7

Time (hours)	Temp. °C	Pressure
2	160	atm
2	200	atm
4	260	atm
10	320	atm
10	360	1 mm

A porous brown polymer, weighing 2.10 g. (~100% of theory), which had a yellow interior, was obtained. The polymer was infusible and insoluble in common solvents.

ii. (DA-29-132) Modification of DA-29-123.

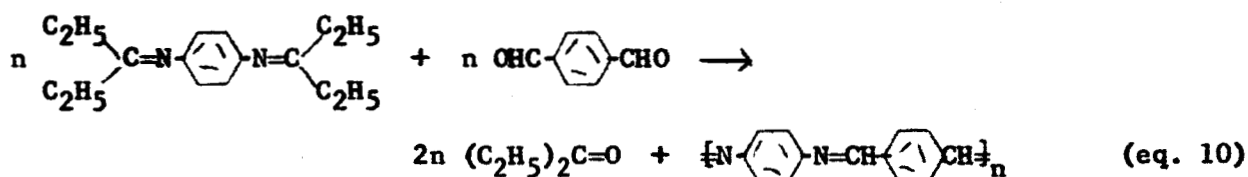
Reaction DA-29-123 was repeated, except that the conditions of polymerization were changed to those listed in Table 8.

Table 8

Time (hours)	Temp. °C	Pressure
4	200	atm
15	290	atm
10	340	atm
10	340	140.0 mm
10	340	0.5 mm

The reaction product was a black-brown porous solid weighing 2.06 g. (~100% yield). Partial foaming and burning took place when the polymer was heated at bunsen flame temperatures.

iii. (DA-29-110) Reaction of D-3-PPFDA with TA.



Into a 50 ml. round-bottomed flask was placed 4.88 g. (0.02 mole) of the bis-Schiff base D-3-PPFDA and 2.68 g. (0.02 mole) TA. As the two compounds were mixed, they changed color from yellow to orange to deep orange. Heat was evolved and the viscosity of the resulting solution increased. Within one-half hour the mixture had become solid and the flask was converted to a melt polymerization system. The reaction mixture was heated at 110-120°C at atmospheric pressure for two hours, during which period, 1.52 g. of the liberated ketone was collected. Heating was continued for sixteen hours, over which period the temperature was raised slowly to 350°C. Then, the solid product was heated for three hours at the same temperature at 7 mm Hg to remove the

non-polymeric materials. When the residue was examined, it was found to contain a multicolored material composed mainly of brown sections with some areas of black. The polymer crumbled easily and was not tough. Some white crystals which had collected in the distilling head during the heating were examined and found by their melting point to be unreacted TA. The weight of polymer obtained was 4.45 g., compared to the calculated theoretical weight of 4.12 g.

iv. (DA-29-115) Modification of DA-29-110 Using Excess D-3-PPFDA.

The bis-Schiff base, D-3-PPFDA, 11.32 g. (0.042 mole) was combined with 4.51 g. (0.03 mole) TA in a 100-ml. round-bottomed flask and the mixture polymerized. The conditions used in this polymerization are given in Table 9.

Table 9

Time (hours)	Temp. °C	Pressure
8	120	atm
10	220	atm
11	220	140 mm
6	220-310	1 mm

At the end of the thirty-five hours of reaction time, 8.24 g. of a black shiny polymer were obtained.

v. (DA-29-116) Modification of DA-29-110 Using Different Conditions.

Instead of the conditions used in DA-29-110 the modifications given in Table 10 were used.

Table 10

Time (hours)	Temp. °C	Pressure
2	180	atm
2	280	atm
2	300	1 mm

Diethyl ketone was collected in the receiver during the period of polymerization. At the end of the six hours of reaction, a 104% yield of a multi-colored polymer was obtained. The polymer was composed of yellow-brown amorphous and glassy regions.

vi. (DA-29-122) Further Modification of DA-29-110.

Using equivalent quantities of dialdehyde and bis-Schiff base, the polymerization was performed under the conditions given in Table 11.

Table 11

Time (hours)	Temp. °C	Pressure
2	130	atm
2	210	atm
10	260	atm
10	320	0.1 mm

The polymer obtained in this reaction was a multicolored, yellow-brown, infusible, insoluble solid. The yield of polymer was 110% of theory.

vii. (DA-29-141) Spontaneous Polymerization of D-3-PPDA and TA.

The bis-Schiff base, D-3-PPDA 2.44 g. (0.01 mole) and 1.34 g. (0.01 mole) TA were placed in a small beaker and mixed vigorously. Ketone rapidly evolved and the reaction was noticeably exothermic. After fifteen minutes the reaction mixture became a solid mass. The reaction was allowed to stand approximately twelve hours after which the yellow-orange polymer was extracted with 95% ethanol for forty-eight hours. The extracted polymer was orange-brown in color and weighed 2.10 g. after drying. The yield was slightly greater than 100%.

Analysis: Calc'd for  $n = \infty$  : C, 81.60; H, 4.85; N, 13.60.

Found : C, 77.58; H, 5.36; N, 12.45.

### b. Solution Polymerizations.

Since difficulty was experienced in obtaining a black polymer in the melt polymerization, it was decided to evaluate benzalaniline as a solvent for the reactions.

#### i. (DA-29-125) Reaction of DBPPDA and TA in the Presence of BA.

(Repeat of DA-29-61 and DA-29-62)

The same general polymerization apparatus was used to polymerize 2.84 g. (0.01 mole) DBPPDA and 1.34 g. (0.01 mole) TA in 3 g. BA. The conditions used are given in Table 12.

Table 12

Time (hours)	Temp. °C	Pressure
2	160	atm
2	200	atm
4	260	atm
10	320	atm
10	320	1 mm
10	400	5 mm

When the reaction was terminated, 2.51 g. (112% theoretical) of a porous black polymer with a brown interior was obtained. The polymer was fusible and soluble in concentrated acetic, formic, and sulfuric acids.

#### ii. (DA-29-112) Polymerization of D-2-PPPDA and TA Using BA.

The bis-Schiff base, D-2-PPPDA, 4.88 g. (0.02 mole) and 2.86 g. of TA were combined in a small round-bottomed flask. The flask was then equipped with a distilling head, nitrogen inlet, condenser, and receiver. This mixture was warmed slightly with a small flame from a bunsen burner until a homogeneous solution was obtained. The color of the solution changed from orange to red. The reaction apparatus was lowered into a metal bath heated to 140°C,

and the temperature was slowly raised to 265°C over a period of two hours, and then maintained at this temperature for ten and one-half hours.

Next, the pressure was reduced to 100 mm and the temperature was raised to 325°C. There was collected 2.10 g. 2-pentanone, together with a very small amount of water. A black material weighing 7.3 g. remained in the reaction flask. Continued heating of the polymer for an additional two hours at 325°C reduced the weight to 6.96 g.

The polymer was ground to a fine powder and extracted with 95% ethanol by means of a Soxhlet extractor for three days. The polymer obtained after this treatment was chocolate brown in color and weighed 6.13 g. Yield of polymer was now 149% on the basis of the amount of D-2-PPDA used.

iii. (DA-29-121) Modification of DA-29-112.

The amount of reagents used in this experiment were identical to those used in DA-29-112. The conditions of polymerization were modified as given in Table 13.

Table 13

Time (hours)	Temp. °C	Pressure
2	160	atm
4	220	atm
4	300	atm
2	320	340 mm
2	320	140 mm
10	320	1 mm
10	360	1 mm

The resulting polymer was black and was produced with a lower yield (114%) than that of DA-29-112. It was also found that the polymer was soluble in concentrated formic and sulfuric acids.

iv. (DA-29-136) Further Modification of DA-29-112.

The conditions of this reaction are shown in Table 14.

Table 14

Time (hours)	Temp. °C	Pressure
4	160	atm
15	230	atm
10	280	atm
15	300	140.0 mm
10	320	0.1 mm

A yellow-brown porous polymer, weighing 6.50 g., was recovered at the end of the reaction. Examination of the polymer showed that it was fusible and that it underwent considerable foaming when heated to about 320°C.

v. (DA-29-138) Further Modification of DA-29-112.

A mixture of D-3-PPFDA, 2.44 g. (0.01 mole), 1.34 g. (0.01 mole) TA, and 4 g. BA were subjected to the carbonyl exchange polymerization using the conditions given in Table 15.

Table 15

Time (hours)	Temp. °C	Pressure
4	160	atm
10	270	atm
10	320	atm
12	320	140.0 mm
10	320	0.3 mm

A hard black polymer which was tough and infusible was recovered from the reaction flask. Weight of the polymer was 3.41 g. or 166% theoretical.

c. Other Solution Polymerizations.

Two experiments were conducted to determine whether the carbonyl exchange

polymerization would occur readily in solution. Two solvents, benzene and acetic acid, were selected for use as examples of polar and non-polar solvents.

i. (DA-29-174) Solution Polymerization in Benzene of TA and DBPPDA.

Equivalent quantities (0.01 mole) of TA and DBPPDA were placed in a round-bottomed flask containing 200 ml. benzene. This reaction mixture was refluxed for seventy-two hours. No change in the solution occurred during this time. Two milligrams of p-toluenesulfonic acid were added and immediately a yellow precipitate formed in the solution in the region of the catalyst. Reflux was continued for ten hours, and when the reaction was cooled, 0.76 g. of a yellow solid precipitated from the solution. The isolated precipitate was found to undergo further condensation, as indicated by color change, on heating.

ii. (DA-29-107) Reaction of D-2-PPPDA and TA in Acetic Acid.

One hundredth of a mole of D-2-PPPDA (2.44 g.) and 25 ml. glacial acetic acid were mixed together in a beaker. Then 1.34 g. (0.01 mole) TA was added. As the mixture was stirred it turned dark red, heat was generated and the viscosity of the solution was increased greatly. After stirring for a short time the reaction mixture solidified. The solid polymer was filtered off and washed with ethanol and distilled water. The final product was dark brown and appeared to be impure. No effort was made to purify the product further.

2. Discussion.

The melt polymerizations using the carbonyl exchange generally gave polymers in which only partial conversion to polymer was obtained. The melt polymerization using the ketonanil monomers and TA showed the expected ease of carbonyl exchange by undergoing spontaneous melt polymerizations at room temperature. The ability of these monomers to undergo exchange readily confirms



the prior conclusion that reactivity as well as volatility of products are the main factors controlling yields in exchange reactions. The development of these monomers provides substrates with reactivities which are far greater than the corresponding benzylidene derivatives.

Polymers which are obtained by both spontaneous melt polymerization and solution polymerization using acetic acid are orange products. Without heating, these polymers have already reached a degree of polymerization which exceeds any that can be obtained by a simple condensation reaction. It is interesting also to note that appropriate aromatic aldehydes are much more active than aliphatic ketones in Schiff base exchange reactions, and that they will replace them easily from their compounds.

Some difficulty was experienced in attempting to produce a black polymer by a reaction between the bis-ketonanils and TA in melt polymerization. Using BA, black polymer could be obtained but retention or incorporation of this substance led to yields in excess of 100%.

The solution polymerization of TA and DBPPDA using benzene as the solvent was shown to give yellow polymers only when catalyzed by p-toluenesulfuric acid. Polymers obtained in this manner are capable of further condensation to give black polymers when they are melted, thus indicating they are of low molecular weight polymers possessing reactive end groups.

#### D. Bis-Schiff Base Exchange Polymerizations.

When two bis-Schiff bases react, one containing an aromatic dialdehyde moiety and the other an aromatic diamino moiety, the resulting product is a stable non-volatile poly-Schiff base. The end groups which are displaced in this reaction combine together to give rise to two equivalents of a more simple volatile Schiff base. The driving force for this reaction can be attributed to two factors; the formation of a very stable polymeric Schiff base and

the removal of the simple volatile Schiff base by distillation. Monomers in which the reactive groups of the diamine and dialdehyde are tied up by aromatic phenyl-CH= or phenyl-N= groups have been discussed in a previous NASA report.<sup>1</sup> Further studies using these monomers are included in this report. The use of monomers in which alkyl groups are used to block the amino functions have not been previously reported. The new monomers, D-3-PPDA or D-2-PPDA were used in the bis exchange polymerization and the results obtained compared with that obtained from completely "aromatic" monomers.

1. Experimental.

a. Melt Polymerization.

i. (DA-29-124) Reaction of DBPPDA and PXDA.

A mixture of DBPPDA 2.84 g. (0.01 mole) and 2.84 g. (0.01 mole) PXDA were placed in a 50-ml. round-bottomed flask equipped with the usual accessories required for distillation polymerization. The conditions given in Table 16 were used during the polymerization.

Table 16

Time (hours)	Temp. °C	Pressure
2	160	atm
2	200	atm
4	260	atm
10	320	atm
10	320	1 mm
10	400	5 mm

On the completion of the polymerization there was obtained a dull black polymer containing some yellow areas. The polymer was non-porous, and brittle; the yield was 112% of theory.

ii. (DA-29-128) Modification of DA-29-124.

The same procedure as described in DA-29-124 was used in this polymerization. The reaction was modified with the conditions of time, temperature, and pressure given in Table 17.

Table 17

Time (hours)	Temp. °C	Pressure
2	180	atm
5	220	atm
10	250	atm
10	280	atm
10	280	140 mm
10	260	7 mm

At the end of the reaction, a yellow polymer was recovered in a 141% yield. The reaction was incomplete, as was shown by heating the yellow oligomer on a spatula in the flame of a bunsen burner, whereby further condensation occurred readily, yielding a black foamed polymeric solid.

iii. (DA-29-130) Modification of DA-29-124 Using Higher Polymerization Temperatures.

A very hard, black polymer which was glass-like in appearance was produced using the same amounts of reagents and equipment as in DA-29-124 under the conditions given in Table 18.

Table 18

Time (hours)	Temp. °C	Pressure
4	200	atm
12	260	atm
15	260	140.0 mm
10	260	140.0 mm
10	320	5.0 mm
10	360	0.5 mm

At the end of the reaction time, 2.46 g. (118% yield) of the polymer was recovered.

iv. (DA-29-149) Modification of DA-29-124, an Attempt to Reduce the Yield.

Table 19 gives the conditions used in the reaction which were the most severe used in these studies.

Table 19

Time (hours)	Temp. °C	Pressure
12	320	atm
11	320	20.0 mm
6	320	1.5 mm
45	420	1.5 mm

A near-to-theoretical yield resulted from the conditions of this experiment and 109% of theory of a black polymer was obtained.

v. (DA-29-186) Reaction of Dibenzylidene-m-phenylenediamine in PXDA.

The two monomers, 2.84 g. (0.01 mole), were mixed together and then placed in a 500 ml. round-bottomed flask. The flask was equipped for distillation polymerization and the reaction flask was immersed in a molten metal bath for the polymerization. The conditions of the reaction are given in Table 20.

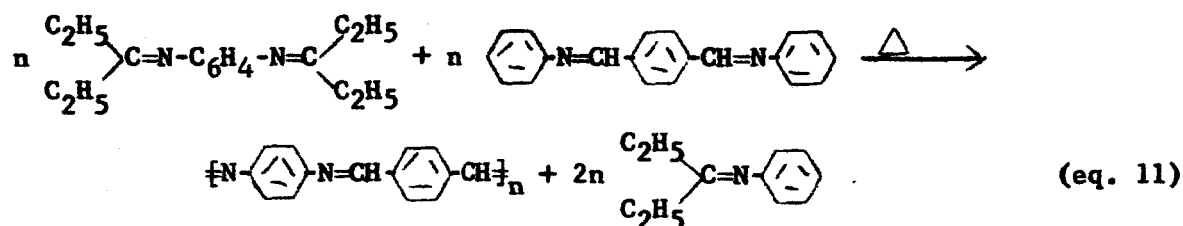
Table 20

Time (hours)	Temp. °C	Pressure
2.5	200-240	atm
3.5	240-300	atm
2.5	300	140 mm
12.0	360	140 mm
3.0	360	1 mm

During the reaction BA was collected in the receiver. At the end of the reaction a shiny glass-like black polymer, yield of 125%, was isolated from the reaction flask.

vi. (DA-29-117) Reaction of D-3-PPFDA and PXDA.

The reaction is given as:



The bis-ketonanil, 4.88 g. (0.02 mole) and 5.68 g. (0.02 mole) PXDA were treated as in the previous experiment. The conditions used during the polymerization are given in Table 21.

Table 21

Time (hours)	Temp. °C	Pressure
5	270	atm
6	340	140 mm

The resulting polymer of this reaction consisted of two parts, a foamed low-density material and a solid glassy material. When the glassy material was heated further, it foamed until it also resembled the first part. The yield of polymer obtained was 133%. When the distillate was examined by means of infrared it appeared to contain a mixture of compounds, but was mostly aniline. No peaks attributable to diethylketonanil were found.

vii. (DA-29-119) Modification of DA-29-117.

The reaction, DA-29-117, was repeated, varying only the conditions of polymerization, as given in Table 22.

Table 22

Time (hours)	Temp. °C	Pressure
10	290	atm
2	290	atm
1	270	340.0 mm
1.5	270	140.0 mm
0.5	300	1.7 mm

The yield of polymer in this reaction was 146%, indicating that large amounts of the monomers remained unreacted, or that the polymer had incorporated in it a large amount of by-product. The color of the reaction product was brown-black, also indicating incomplete reaction.

viii. (DA-29-120) Repeat of DA-29-117.

The conditions used in this polymerization are given in Table 23.

Table 23

Time (hours)	Temp. °C	Pressure
10	325	atm
4.5	325	140.0 mm
3	325	1.7 mm
17	360	1.7 mm

In this experiment, the yield of black polymer was 110%, and considerable foaming of the polymer was noted when this fusible polymer was heated on a spatula at bunsen flame temperatures.

ix. (DA-29-139) Further Modification of DA-29-117.

The temperature of this reaction was higher than that of DA-29-117, and the time of reaction was increased to produce an infusible polymer. The modified conditions are given in Table 24.

Table 24

Time (hours)	Temp. °C	Pressure
4	220	atm
15	310	atm
10	320	140.0 mm
14	320	1.0 mm
25	380	1.0 mm
20	380	0.5 mm

A black, porous, non-fusible polymer, weighing 1.73 g., 84% yield was obtained in this experiment. Some volatilization of the reagents appeared to have taken place during the reaction. The distillate contained only aniline.

b. Solution Polymerizations.

i. (DA-29-140) Reaction of D-3-PPDA.

Benzalaniline, 3 g., were added to a mixture of 2.44 g. (0.01 mole) bis-ketonanil and 2.84 g. (0.01 mole) PXDA. The reaction mixture was then polymerized under a nitrogen atmosphere and the reaction conditions are given in Table 25.

Table 25

Time (hours)	Temp. °C	Pressure
4	220	atm
15	310	atm
10	320	140.0 mm
14	320	1.0 mm
5	380	1.0 mm
20	380	0.5 mm

The reaction product was solid at the end of the reaction time, and a black, shiny solid polymer was obtained, which weighed 2.89 g., 140% yield.

### c. Other Solution Polymerizations.

#### i. (DA-29-155) Reaction of DBPPDA and PXDA in Ethanol.

Two-tenths of a gram, 0.2 g., of each of the two bis Schiff bases were dissolved separately, each in 200 ml. absolute alcohol. The two solutions were combined in a 500-ml. beaker at room temperature. The solution was stirred for two days by means of a mechanical stirrer. No change was observed in the yellow solution after this time. About 0.25 g. zinc chloride was added as a catalyst and in two hours a yellow precipitate began to collect. The amount of precipitate increased over the next twenty-four hours; then it was collected by filtration. When a melting point of the precipitate was taken, the precipitate began to melt at about 200°C, then it underwent a gradual change in color from yellow to red to black. To check possible complex formation with zinc chloride, 0.25 g. of zinc chloride was added to each of the two beakers containing 0.2 g. of each of the monomers in 200 ml. ethanol. After two days no change had occurred in either of the beakers, and it was concluded that the isolated precipitate was not a complex of the monomers with zinc chloride.

#### ii. (DA-29-157) Repeat of DA-29-155 Using p-Toluenesulfonic Acid as a Catalyst.

Two separate 200-ml. solutions each containing 0.2 g. of each of the monomers were mixed. After one hour, no reaction had occurred; then 2 mg. of p-toluenesulfonic acid was added. Within another hour, a yellow-orange substance began to precipitate from solution. After separating the precipitate by filtration and drying it, the weight was 0.082 g. This substance had no melting point but darkened readily on strong heating. Infrared spectroscopy showed the characteristic Schiff base bands, and the spectrum of this compound resembled closely the spectra of low molecular weight polymers obtained in condensation reactions.



## 2. Discussion.

The melt polymerizations of the bis-exchange reaction give products which are generally of a higher molecular weight than those obtained by any other polymerization method. This is due to the action of benzalaniline which is produced during the reaction. The yields, however, generally tended to be much greater than 100%. No spontaneous reaction of these monomers was noted as in the carbonyl exchange reaction. Polymerizations employing the bis-ketonanils as one of the monomers proceeded quite easily, yielding glassy black materials in many cases. The expected by-product, diethylketonanil, in the reaction of the bis-ketonanil with PXDA, was never isolated. It is possible that it is unstable decomposing under the high temperatures used in the reaction.

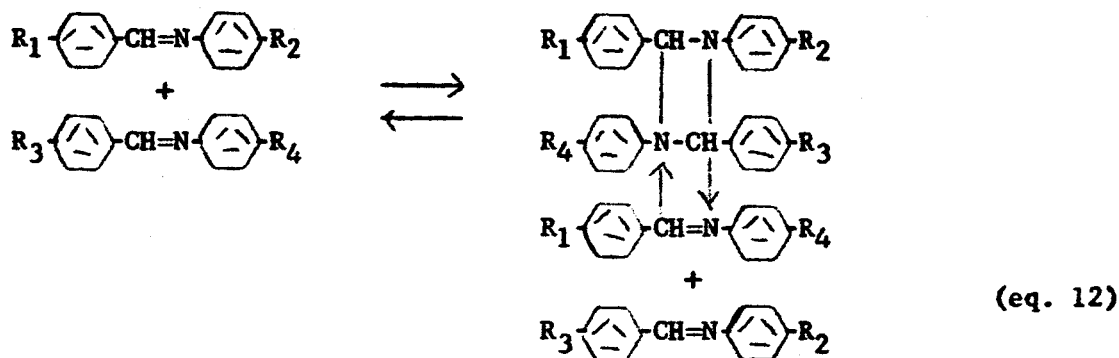
The use of a large excess of benzalaniline in the bis-exchange polymerizations, as in DA-29-140, lends little or no advantage to this reaction. Benzalaniline tends to be incorporated into the polymer to a considerable degree, and is difficult to remove.

Solution polymerizations using the aromatic monomers, DBPPDA and PXDA, show that the bis Schiff base exchange can occur even at low temperatures when catalyzed either by zinc chloride or p-toluenesulfonic acid. The facility with which this reaction proceeds is surprising, as is the ability of the resulting polymers to be further polymerized to the black stage, a behavior which is not possible with the normal condensation polymers.

### E. Thermal Stability of Monomeric Schiff Bases and Mixtures with Monoacetal.

If it is assumed that the reason for the higher-than-theoretical yield of polymer is due to adduct formation between the polymer and a monomeric Schiff base, which may be present in the system either as a solvent or as a reaction by-product, then heating at higher temperatures would be expected to break the adduct and eliminate the monomeric Schiff base. It would also be expected that the course of the dissociation of the adduct would be determined by the thermodynamics of the system.

In other studies, Ingold suggested<sup>14,15</sup> that Schiff bases form four-membered rings by addition across the  $-C=N-$  bond of the Schiff bases to yield structures which were not thermally stable and which, on heating, yield derived Schiff bases as follows:



Accordingly, and in view of Ingold's studies, polymerizations and post heatings of polymerization products were conducted at higher temperatures for the systems in which the yield of polymer exceeded the theoretical values. Of major interest to this project are the polymeric Schiff bases prepared from acetals as one of the reactants.

Prior to undertaking the studies on the polymers at higher temperatures, the thermal stabilities of Schiff bases, with and without acetal, were evaluated. Most of the stability experiments were performed at 160°C for

fourteen hours, and then 260°C for seventy-nine hours in sealed tubes which had been degassed and sealed at  $3 \times 10^{-5}$  mm Hg pressure, except experiment DA-26-236, in which variations in time and temperature were made. The reaction systems and the results are summarized in Table 26.

1. Experimental.

a. (DA-26-212) Stability of Benzaniline (BA).

Five grams of benzaniline (m.p. 49-50°C) were charged in an ampoule and degassed under  $3 \times 10^{-5}$  mm Hg pressure for five hours. After sealing, the ampoule was heated at 160°C for fourteen hours and then at 260°C for seventy-nine hours in a heated molten metal bath. The color of the BA did not change as a result of this extensive heating at high temperature; and the melting point of the recovered heated BA, without recrystallization, was 49-51°C. The IR spectra of the BA before and after the heating were identical.

b. (DA-26-213) Stability of a Mixture of BA and DBPPDA.

Two grams of DBPPDA (m.p. 139-140°C) and 2.5 g. of BA were heated together in a sealed ampoule under the same conditions as used in DA-26-212. There was no change in either the color or the IR spectrum of the mixture before and after heating. From the heated mixture, 1.9 g. of DBPPDA (m.p. 140°C) were recovered by recrystallization from ethyl alcohol and its IR spectrum was identical with that of authentic DBPPDA.

c. (DA-26-214) Stability of a Mixture of BA and PXDA.

Two grams of PXDA (m.p. 161°C) and 2.5 g. of BA were heated under conditions identical to DA-26-212. On heating, the color of the mixture changed from pale yellow to golden yellow, but there was no change in the IR spectrum of the mixture before and after the heating. On recrystallizing the mixture from alcohol, 1.7 g. (85%) of PXDA, m.p. 160°C, were recovered and

its IR spectrum was identical with that of an authentic sample of PXDA.

d. (DA-26-236) Stability of Mixture of BA and Benzylidenediethyl Ether.

A mixture of 5 g. benzalaniline and 5 g. benzylidenediethyl ether (BDE), was heated at 180°C for twelve hours, at 230°C for ten hours, and then at 240°C for twelve hours. The IR spectra of the mixture during and after the heating was identical to that taken before heating.

Table 26

Effect of Heating on IR of Schiff Bases

Exper. No.	Reaction System	Wt. Gr.	IR Change
DA-26-212	$C_6H_5CH=NC_6H_5$	5.0	None
DA-26-213	$C_6H_5CH=NC_6H_5$	2.5	None
	$C_6H_5CH=N-C_6H_4-N=CHC_6H_5$	2.0	
DA-26-214	$C_6H_5CH=NC_6H_5$	2.5	None
	$C_6H_5N=CH-C_6H_4CH=NC_6H_5$	2.0	
DA-26-236	$C_6H_5CH=NC_6H_5$	5.0	None
	$C_6H_5CH(OC_2H_5)_2$	5.0	

2. Discussion.

From the above results it may be concluded that the Schiff bases are thermally stable and indifferent to each other and to an acetal, except that they are capable of undergoing an acetal exchange, as shown<sup>3</sup> previously.

F. Reaction of p-Xylylidenetetraethyl Ether, Dibenzylidene-p-phenylenediamine in Benzalaniline at Temperatures in Excess of 300°C.

1. Polymerization at 300°C.

In Section E above, reaction or adduct formation was not found to occur in the monomeric systems studied. Studies of this kind were extended to polymerization systems involving the polyfunctional molecules p-xylylidene-tetraethyl ether (XTEE) with DBPPDA, in which BA would be used as a solvent. The reactions were performed at elevated temperatures under a nitrogen at-

mosphere at reduced pressure. The reaction conditions and results are summarized in Table 27.

Table 27  
Reactions of XTEE and DBPPDA Under Various Conditions

Exper. No.	Reaction Temp. °C/mm Hg Pressure	Reaction Intervals (hours)	Polymer Yield %	Appearance of Polymer
DA-26-211	200-220/14 300-340/14+2.5	42.5 24.5	132	black, partially brown
DA-26-215	280-300/760 280-300/300+100 290-300/2.5	6.5 16.0 6.0	137	brown
DA-26-229	170-180/500 215-240/340+140 300-350/1.5	0.5 17.0 12.0	300	black-brown
DA-26-232	220/140 220-270/140+1 300-320/1	4.0 12.0 4.0	185	black

a. Experimental.

i. (DA-26-211) Reaction of DBPPDA and XTE in BA.

A mixture of 3.027 g. of DBPPDA, 3.0 g. of XTE and 3 g. of BA was polymerized in a suitable reaction flask according to the following cycle:

17.0 hours	at 220°C	at 200 mm Hg pressure;
4.5 hours	at 220°C	at 80 mm Hg pressure;
9.0 hours	at 220°C	at 50 mm Hg pressure;
12.0 hours	at 220°C	at 14 mm Hg pressure;
5.5 hours	at 300°C	at 14 mm Hg pressure;
19.0 hours	at 300°C	at 2.5 mm Hg pressure.

During the reaction 3.9 g. of distillate was collected in a water-cooled receiver and it was found to contain BA and BDE. In a CO<sub>2</sub> trap, 0.6 g. of ethyl alcohol was recovered. The yield of black polymer containing brownish areas was 2.9 g. (132% yield).

ii. (DA-26-215) Repeat of DA-26-211 Under Different Conditions.

The same amount of materials were used as in DA-26-211 but were reacted under the following conditions:

6.5 hours	at 280-300°C	at 760 mm Hg pressure;
14.0 hours	at 280°C	at 300-200 mm Hg pressure;
2.0 hours	at 300°C	at 100 mm Hg pressure;
6.0 hours	at 300°C	at 2.5 mm Hg pressure.

The total weight of distillate was 1.9 g. and the weight of the brown polymer was 3 g. (137% yield). The distillate contained BA and BDE.

iii. (DA-26-229) Repeat of DA-26-211 Under Different Conditions.

The same reagents and amounts of materials were used as in DA-26-211 but they were reacted under the following conditions:

0.5 hours	at 170-180°C	at 500.0 mm Hg pressure;
0.5 hours	at 215-230°C	at 340.0 mm Hg pressure;
0.5 hours	at 230°C	at 140.0 mm Hg pressure;
16.0 hours	at 240°C	at 40.0 mm Hg pressure;
12.0 hours	at 300-350°C	at 1.5 mm Hg pressure.

The distillate amounted to 2.1 g. and was shown to contain BDE. The weight of brown-black polymer was 6.5 g. (300% yield).

iv. (DA-26-232) Repeat of DA-26-211 Under Different Conditions.

A mixture of 10.09 g. of DBPPDA, 10 g. of XTE and 10 g. of BA was polymerized under the following conditions:

4.0 hours	at 220°C	at 140 mm Hg pressure;
1.0 hours	at 220-250°C	at 140 mm Hg pressure;
11.0 hours	at 250-270°C	at 1 mm Hg pressure;
4.0 hours	at 300-320°C	at 1 mm Hg pressure.

During the reaction a total of 12.3 g. of distillate was collected. The polymer was black and weighed 13.6 g. (185% yield).

v. (DA-26-235) Repeat of DA-26-211 Under Different Conditions.

A mixture of 13.18 g. of DBPPDA, 13.23 g. of XTE (3% excess) and 13.0 g.

of BA was polymerized under the following conditions:

0.7 hours	at	200°C	at 30 mm Hg pressure;
0.8 hours	at	210°C	at 50 mm Hg pressure;
1.0 hours	at	210°C	at 40 mm Hg pressure;
3.0 hours	at	240°C	at 40 mm Hg pressure;
10.0 hours	at	250-260°C	at 14 mm Hg pressure;
8.0 hours	at	300°C	at 1 mm Hg pressure.

The weight of the distillate amounted to 20.7 g. and the weight of the polymer, which was brown, amounted to 17.1 g. (176% yield).

#### b. Discussion.

It will be observed in the data summarized in Table 27 that the yield of polymers in these polymerizations conducted in the vicinity of 300°C, is always higher than 100% of theory, indicating retention of by-products or of BA. The distillates in these polymerizations were subjected to IR analyses and benzylidenediethyl ether was found in all of them, indicating that some acetal exchange had occurred with benzalaniline, and that the polymer chains were telomerized by the aniline moiety.

Within the temperature range used in the polymerizations, the yields were not markedly reduced with slight increases in temperature. It seemed obvious that higher temperatures would be required to eliminate materials retained in the polymer.

#### 2. Post-Heatings of Polymerization Products.

Post-heating at elevated temperatures of some of the polymers listed in Table 27 were performed in an attempt to eliminate adduct components or retained reagents from the polymers. The heated polymers are coded with an H. The conditions and the final yields reached by post-heating under the specified conditions are summarized in Table 28.

Table 28

## Yields of Post-Heated Polymers

Exper. No.	Heating Temp. °C /mm Hg Pressure	Heating Time (hours)	Polymer Yield %	
			Before Heating	After Heating
DA-26-211.H	320-250/2-3	60	132	103
DA-26-215.H	320-350/2-3	60	137	119
DA-26-232.H	320-350/1	24	185	166
DA-26-233.H	340-350/1.0	36	140	124
DA-26-235.H-1	360-420/0.5	10	176	149
DA-26-235.H-2	360-420/0.2	45	176	146
DA-26-235.H-3	360-420/0.2	74	176	145
DA-26-237.H-1	360-420/0.5	10	156	130
DA-26-237.H-2	360-420/0.2	45	156	123
DA-26-237.H-3	360-420/0.2	74	156	118

a. Experimental.i. DA-26-211.H.

Polymer DA-26-211, 0.9087 g., was heated at 320-350°C for sixty hours under a flow of nitrogen at 2 ~ 3 mm Hg pressure. Yield, 0.7038 g.; weight decrease, approximately 23% of original weight.

ii. DA-26-215.H.

Polymer DA-26-215, 1.0143 g., was heated at 320-350°C for sixty hours under a flow of nitrogen at 2 ~ 3 mm Hg pressure. Yield, 0.8913 g.; weight decrease 12% of original weight.

iii. DA-26-232.H.

Polymer DA-26-232, 2.823 g., was heated under 1 mm Hg pressure of nitrogen for twenty-four hours. Yield, 2.543 g.; weight decrease approximately 10% of original weight.

iv. DA-26-233.H.

Polymer DA-26-233, 1.1795 g., was heated at 340-350°C for thirty-six



hours under 10 mm Hg pressure of nitrogen. Yield, 1.003 g.; weight loss approximately 15% of original weight.

v. DA-26-234.H-1.

Polymer DA-26-234, 1.401 g., was heated at 340-350°C for twelve hours under 1 mm Hg pressure of nitrogen. Yield, 1.000 g.; weight decrease, approximately 40% of original weight.

vi. DA-26-234.H-2.

Polymer DA-26-234, 1.2655 g., was heated at 340-350°C for thirty-six hours under 10 mm Hg pressure of nitrogen. Yield, 0.023 g.; weight decrease, approximately 11% of original weight.

vii. DA-26-235.H.

Polymer DA-26-235 was used as the sample; all heatings were performed at 360°C under a nitrogen flow, and in some cases the distillate was collected and identified.

Exper. No.	Initial Weight gr.	Final Weight gr.	Weight Loss %	Distillate
DA-26-235.H-1	2.332	1.981	15.0	DA-26-235.H-1-D
DA-26-235.H-2	3.009	2.483	17.0	not collected
DA-26-235.H-3	2.003	1.656	17.5	DA-26-235.H-3-D-1 DA-26-235.H-3-D-2

viii. DA-26-237.H.

Polymer DA-26-237 was used as the sample; all heatings were performed at 360°C under nitrogen flow, and the distillates collected and identified.

Exper. No.	Initial Weight gr.	Final Weight gr.	Weight Loss %	Time Hours	Distillate
DA-26-237.H-1	2.1110	1.7715	16	10	DA-26-237.H-1-D
DA-26-237.H-2	2.668	2.155	21	45	DA-26-237.H-2-D
DA-26-237.H-3	1.757	1.331	24	75	DA-26-237.H-3-D-1 DA-26-237.H-3-D-2 DA-26-237.H-3-D-3 DA-26-237.H-3-D-4

#### b. Discussion.

The data in Table 28 indicates that post-heating at temperatures above 300°C does cause a reduction in the high yield toward the direction of theoretical yields. Also, it may be noted that longer periods of time at highly reduced pressures tend to reduce the yield more effectively than at lower pressures. They may be indicative that the elimination is diffusion-controlled and this would be expected to be low for large by-product molecules. The reduction may be due not only to elimination of retained by-products or BA solvent, but also to an increase in the degree of polymerization.

#### 3. Identification of Distillates Due to Post-Heating.

It was hoped that the nature of the chemical processes that occurred during post-heating could be resolved by identifying the distillates collected during the post-heating period. The distillates were collected and their composition determined from their IR spectra. The distillates from the heated polymers are identified by the letter D. The results are summarized in Table 29.

From the data of Table 29 no positive conclusion can be made concerning the dissociation reaction of four-membered ring adducts as suggested by Ingold<sup>14,15</sup> because the yields are still higher than the theoretical values,

Table 29

## Identification of Distillates Obtained During Post-Heating of Polymers

Exper. No.	Reaction Condition °C/mm Hg Pressure : Hours	Kind of Eliminated Material
DA-26-235.H-1-D	360-420/0.5 : 10	$C_6H_5CH=N-C_6H_4-N=CH-C_6H_5$ $H_2N-C_6H_4-NH_2$ and small amount of $C_6H_5NH_2$ and $C_6H_5CH=N-C_6H_5$
DA-26-235.H-3-D-1	360-390/0.2 : 35	$C_6H_5CH=N-C_6H_4-N=CH-C_6H_5$ and small amount of $C_6H_5CH=N-C_6H_5$ , $H_2N-C_6H_4-NH_2$ and $C_6H_5NH_2$ (?)
DA-26-235.H-3-D-2	360-380/0.2 : 24 400-420/0.2 : 15	$C_6H_5CH=N-C_6H_4-N=N-C_6H_5$ , $C_6H_5COOH$ , $H_2NC_6H_4NH_2$ , $C_6H_5CH=NC_6H_5$ , $C_6H_4(COOH)_2$ , $C_6H_5NH_2$ (?) and aldehydes (?)
DA-26-237.H-1-D	360-420/0.5 : 10	almost all $H_2NC_6H_4NH_2$
DA-26-237.H-2-D	360-420/0.5 : 45	$H_2NC_6H_4NH_2$ and small amount of $C_6H_5NH_2$ , $C_6H_5CH=NC_6H_5$ and $C_6H_5CH=NC_6H_4N=CHC_6H_5$
DA-26-237.H-3-D-1	360-380/0.2 : 5	$H_2NC_6H_4NH_2$
DA-26-237.H-3-D-2	360-380/0.2 : 30	$C_6H_5CH=NC_6H_4N=CHC_6H_5$ , $H_2NC_6H_4NH_2$ , $C_6H_5CH=NC_6H_5$ and $C_6H_5NH_2$
DA-26-237.H-3-D-3	360-380/0.2 : 24	$C_6H_5CH=NC_6H_4N=CHC_6H_5$ and $H_2NC_6H_4NH_2$
DA-26-237.H-3-D-4	400-420/0.2 : 15	Wet resinous material; no -NH <sub>2</sub> and little of -C <sub>6</sub> H <sub>4</sub> -

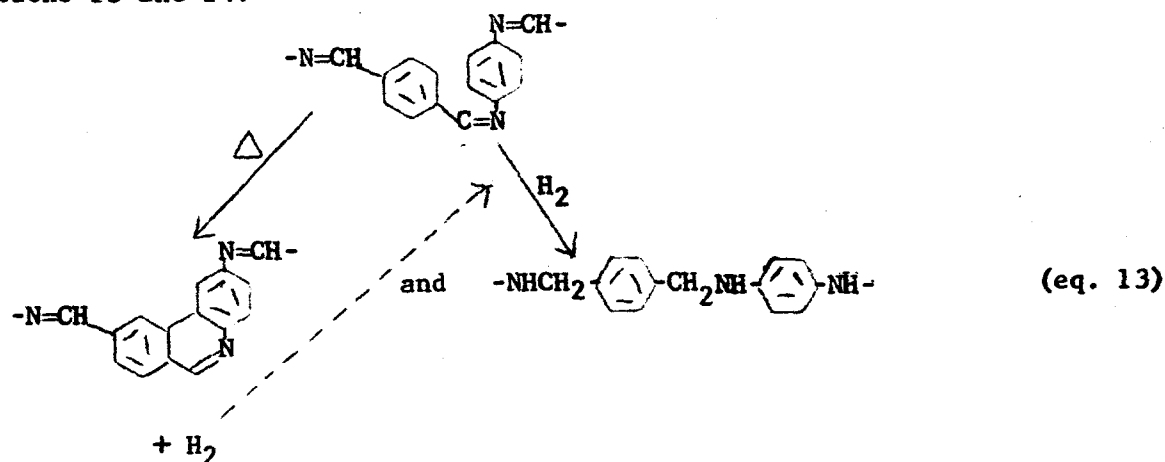
and the amount of eliminated  $C_6H_5CH=NC_6H_5$  is always less, on a molar basis, than the other compounds found in the distillate. Each compound found in the distillates collected during the post-heating may be considered as having an origin as follows:

- i) Originally present in the polymer system as a solvent or as a reaction product;

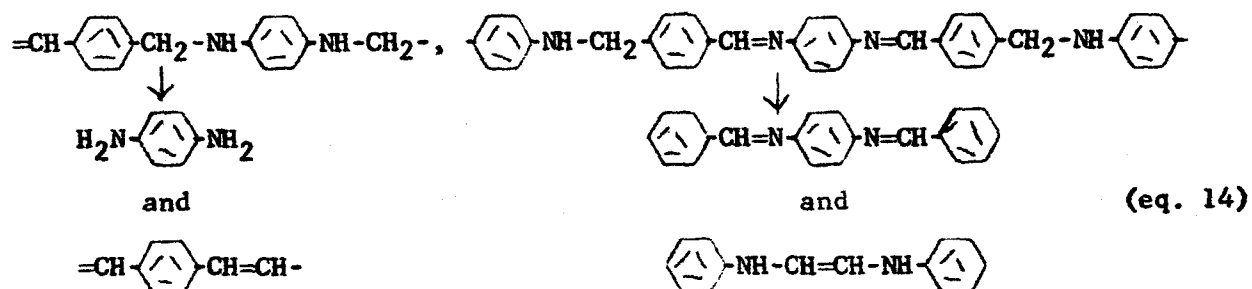
ii) It arises as a product eliminated from adducts, including four-membered ring structures.

b.  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$  and  $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$ .

G.M. Badger et al have reported<sup>16</sup> that benzalaniline in solution in concentrated sulfuric acid is photochemically converted to a mixture of phenanthridine and benzylaniline. If this type of reaction occurs, even to low degree in Schiff bases polymerizations, or during post-heating at higher temperatures, the polymers obtained would undergo some ring closures, and then from such units  $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$  and  $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$  could be eliminated as by-products of thermal decomposition by such reactions as shown in equations 13 and 14.



Then,  $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$ ,  $\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CHC}_6\text{H}_5$  may be produced by pyrolysis, thus



In any case, the data and evidence indicates that scission of the polymer chain is not significant either during a polymerization or post-heating at a higher temperature.

#### 4. IR Spectra of Polymers Before and After Post-Heating.

The infrared spectra of a number of polymers were recorded before and after post-heating to determine whether or not structural changes occurred as a result of post-heating. The IR spectra of polymer DA-26-211 before and after post-heating are shown in Figures 1 and 2 respectively, and of polymer DA-26-215 before and after heating in Figures 3 and 4 respectively.

The expected decrease in the  $C_6H_5$ -absorption band which would follow the elimination of adduct products is not observed. Also significant changes could not be observed in the spectra of the polymers before and after post-heating.

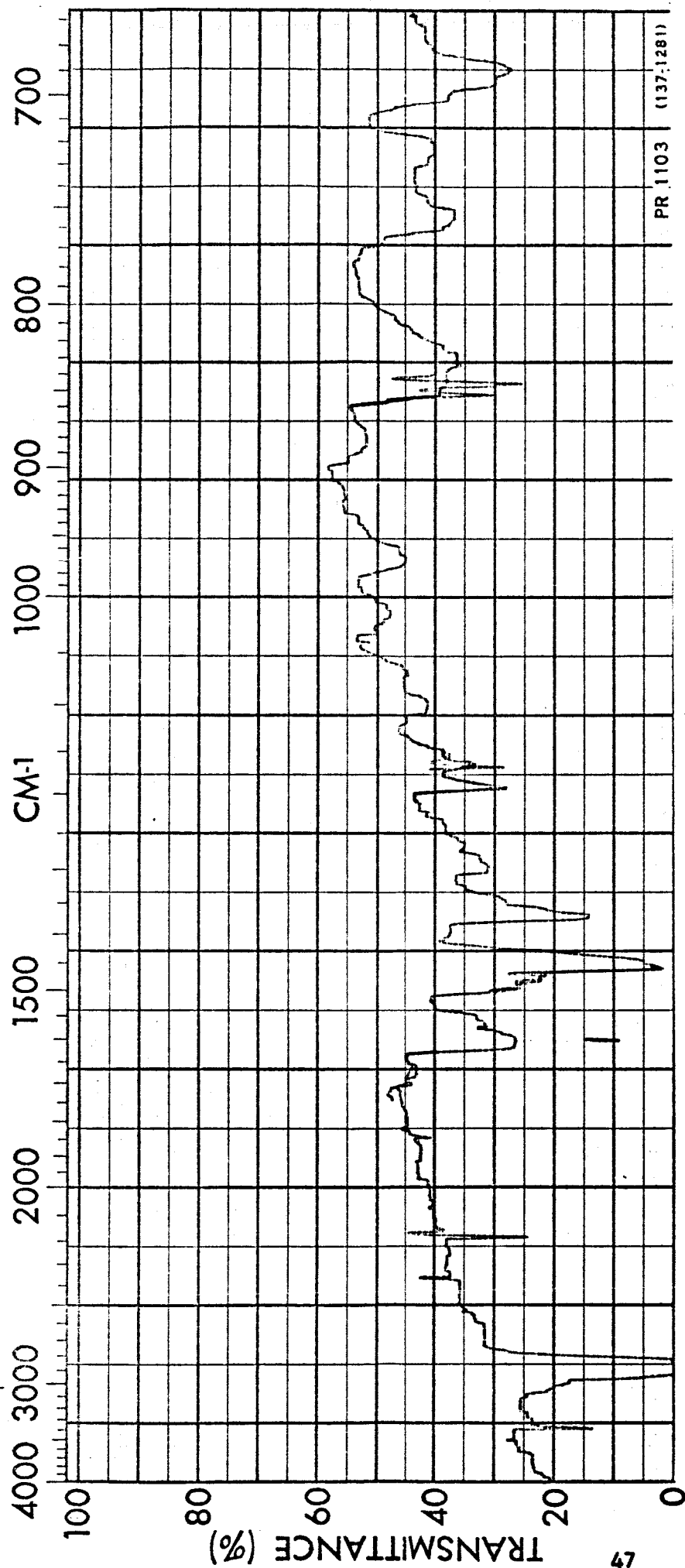
#### 5. Solvent Extraction of Polymers.

In attempts to determine the origin of the distillates obtained by post-heating of the polymers, two typical polymers were subjected to extraction and the extracted materials characterized by their IR spectra and compared with materials collected during post-heating. Extractions were performed on polymers DA-26-235 and DA-26-237 in a Soxhlet apparatus for eighty hours with alcohol as an extractant; the results are summarized in Table 30.

Table 30

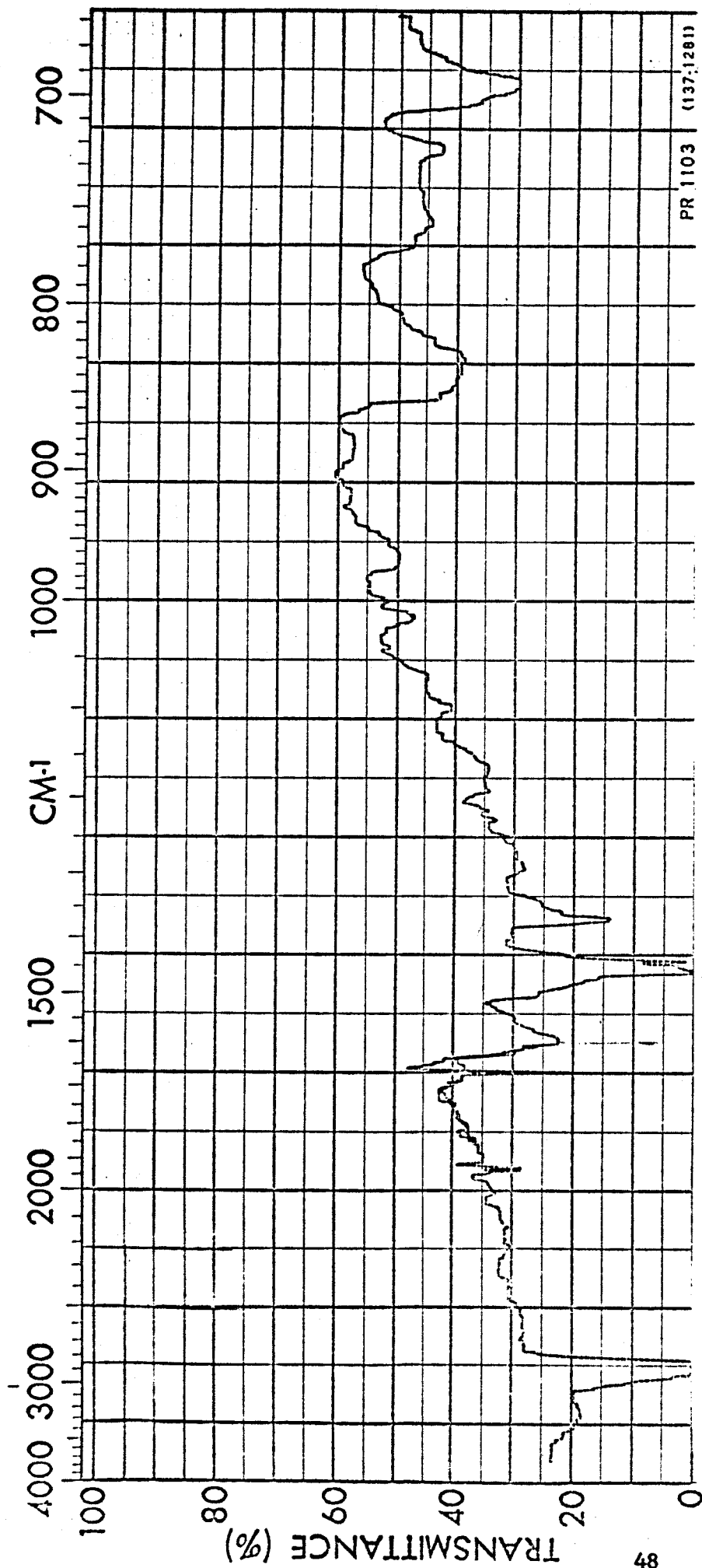
Results of Extraction of Polymers with Ethyl Alcohol

Exper. No.	Polymer Used; Amount	Weight Loss %	Final Yield Based on Weight Loss %
DA-26-235E	DA-26-235; 1.613 g.	15	149
DA-26-237E	DA-26-237; 1.106 g.	15	132



Infrared Spectrum of DA-26-211 Before Heating  
(Mineral Oil Mull)

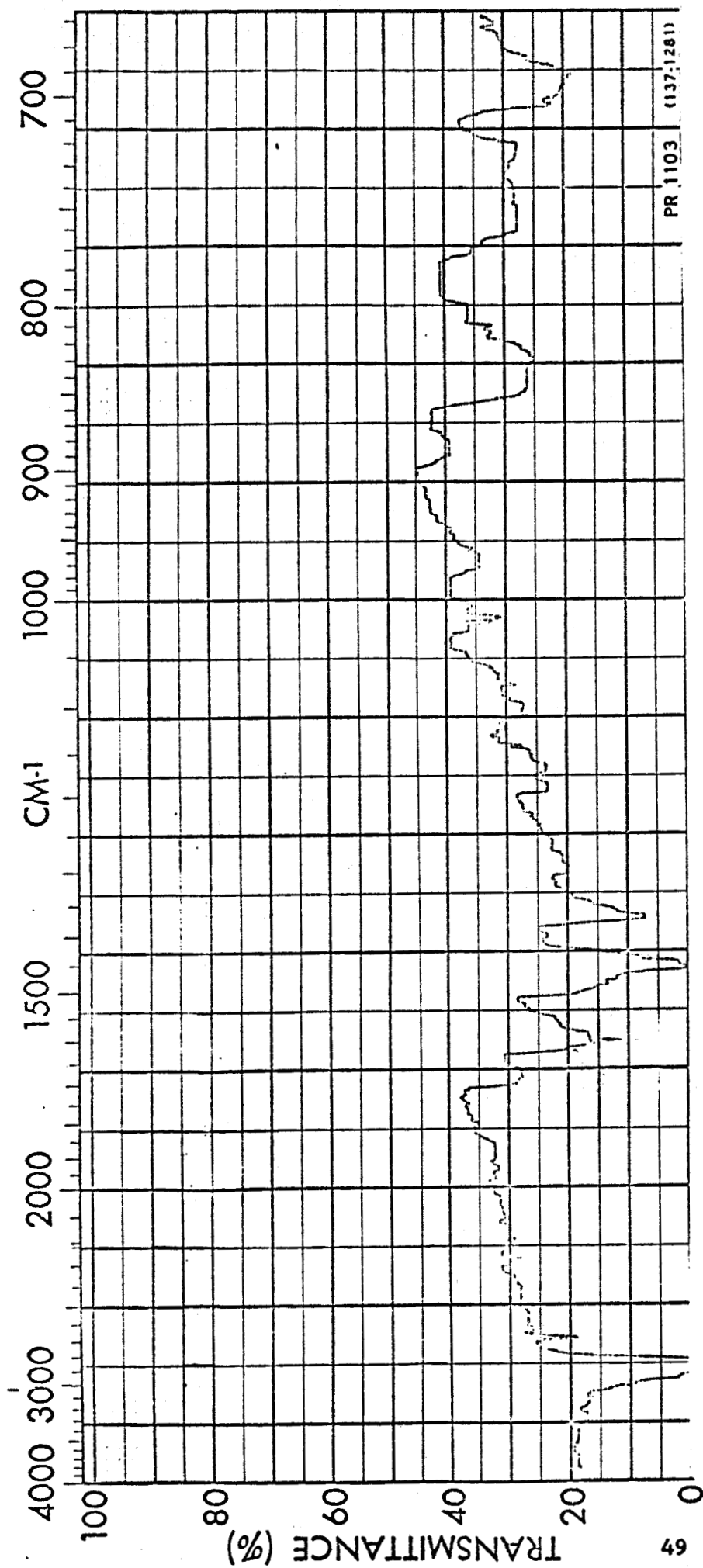
Figure 1



Infrared Spectrum of DA-26-211 After Heating

(Mineral Oil Mull)

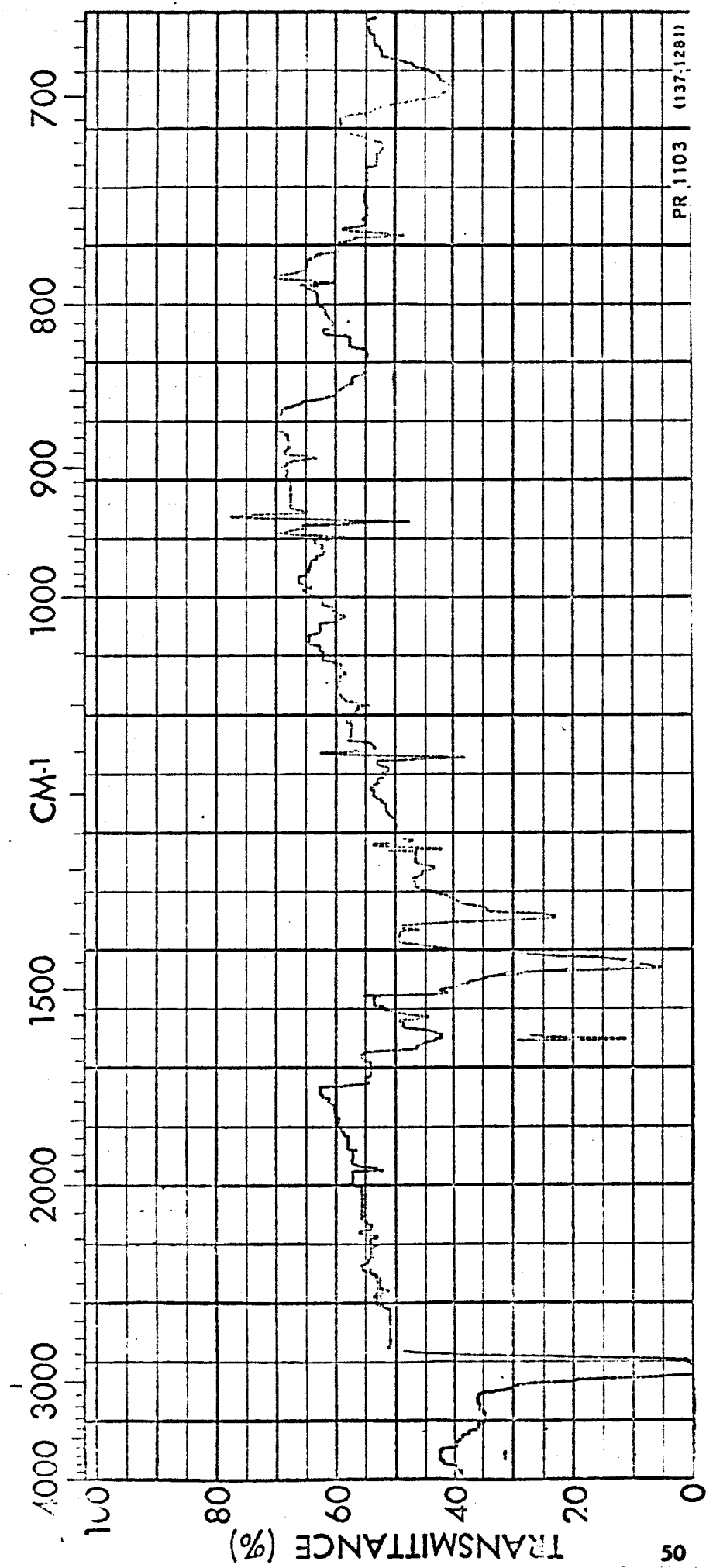
Figure 2



Infrared Spectrum of DA-26-215 Before Heating  
(Mineral Oil Mull)

Figure 3





Infrared Spectrum of DA-26-215 After Heating  
(Mineral Oil Mull)

Figure 4

a. Experimental.

i. (DA-26-235-E) Extraction of DA-26-235.

Polymer DA-26-235 was treated in a Soxhlet apparatus for eighty hours using alcohol as the solvent. The polymer was weighed dry before and after the extraction, and the weight of the extracted materials weighed after evaporation of its alcohol solution. The results are as follows:

initial weight of polymer	1.613 g.
final weight of polymer	1.372 g.
weight loss	0.241 g.
weight loss %	15.0
amount of extract	0.234 g.

ii. (DA-26-237-E) Extraction of DA-26-237.

Polymer DA-26-237 was extracted under the same condition used in DA-26-235-E. The IR spectrum of the extracted materials were recorded after recovery by evaporation from the alcohol solution. The results are as follows:

initial weight of polymer	1.106 g.
final weight of polymer	0.945 g.
weight loss	0.161 g.
weight loss %	15.0
amount of extract	0.153 g.

b. Discussion.

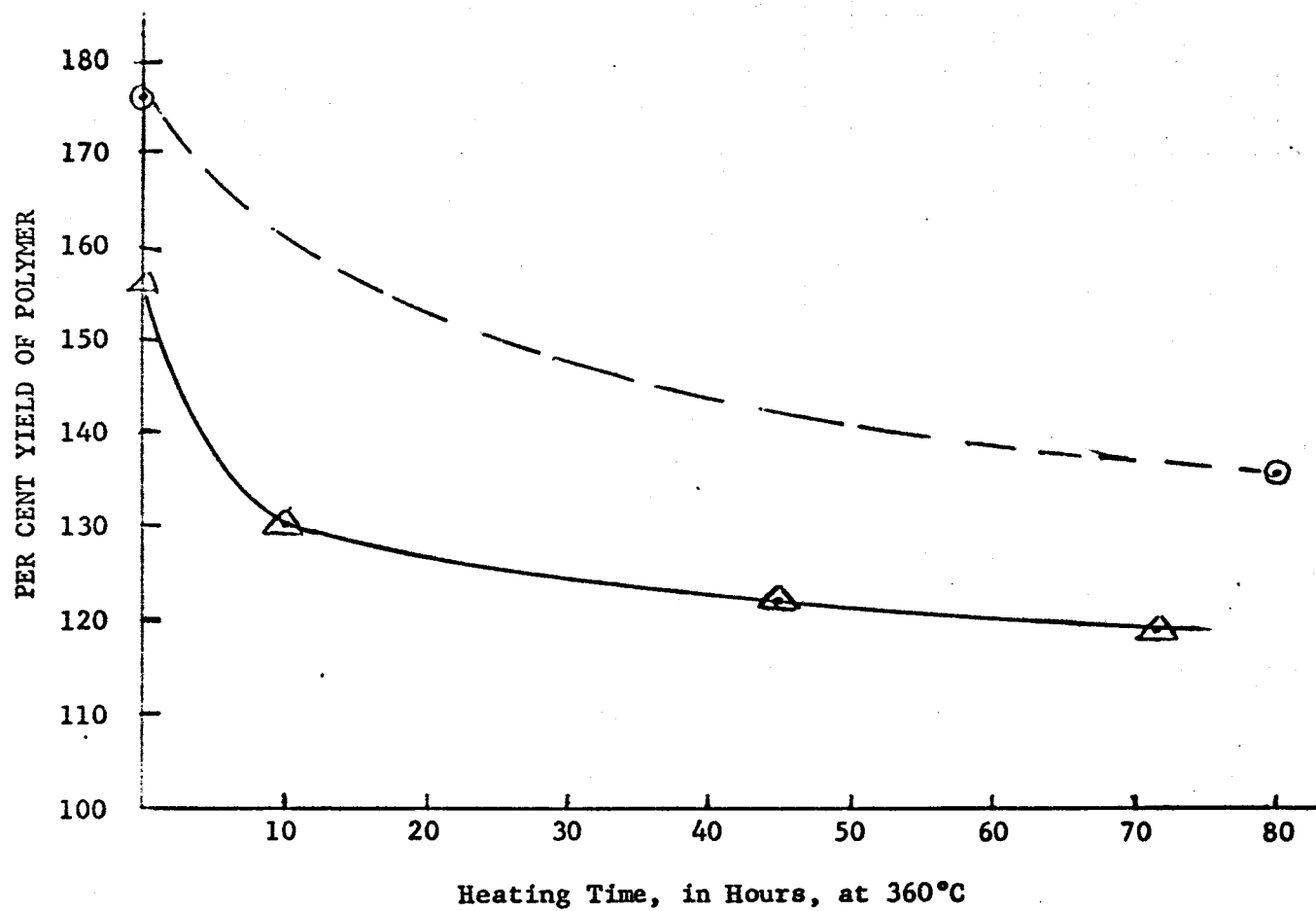
The IR spectrum of the material extracted from DA-26-237 showed that it consisted of  $C_6H_5CH=NC_6H_5$ ,  $C_6H_5CH=NC_6H_4N=CHC_6H_5$ ,  $H_2NC_6H_4NH_2$  and  $C_6H_5NH_2$ ; and the shape of its absorption spectrum was almost identical to that of the distillates obtained in the early stages of post-heating of polymers DA-26-237-H and DA-26-235-H.

The decrease in yield on heating is shown in a typical curve in Figure 5, in which the yield is compared with the value obtained by extraction. Accordingly, it may be concluded that most of the product eliminated in post-heating are not the result of the heat dissociation of adducts or of by-products, at least until the range of the weight loss is about 15%, but that they are materials which are formed in the early stages of polymerization and distributed through the polymer mass.

#### 6. General Discussion.

The yield of polymer obtained by reacting XTE and DBPPDA at low temperatures is much higher than the calculated theoretical yield. When the polymerizations are conducted at higher temperatures, or the polymer is post-heated, the yield of the polymer is reduced. However, the yield of polymers under the conditions evaluated are still above one hundred per cent. The over-yield may be due to the presence of adducts but their existence could not be proven. The high yield can be attributed also to an incomplete polymerization reaction, as shown by the lower yield obtained by post-heating in contrast to the yield of polymer obtained by extraction.

The weight decrease that occurs during the early stages of post-heating a polymer at temperatures higher than the low temperature of the preparation is due to the elimination of by-products formed at the lower temperatures. The amount of decomposition that occurs on heating at higher temperatures is negligible, if any; and if it does occur in molecular weight, since cyclization would occur, is not significant. To more nearly approach theoretical yields, extended heating at temperatures of about 400°C at very low pressures appears to be necessary. This is predicted on the bases of the extremely high melt viscosity of the polymers of relatively low molecular weight, and the solid nature of polymers of slightly higher molecular weight. In such



△ Decrease in Polymer Yield of DA-26-237 on Heating  
○ Yield on Extraction

Figure 5

a medium of high viscosity, the collision factor would be reduced and the products of condensation would have to diffuse out of a medium of high viscosity. The process, therefore, is diffusion controlled. This behavior, experienced in the polymerization of XTE with DBPPDA alone or in the presence of BA confirms the similar experiences of the bis-exchange reactions of DBPPDA and PXDA.

G. Polymerization of Xylylidenetetraethyl Ether with m-Phenylenediamine in Benzalaniline.

When m-phenylenediamine (MPDA) and its derivative are used instead of p-phenylenediamine (PPDA) as the source of the amine moiety in a polymeric Schiff base, one would expect that the configuration of the polymer derived from the MPDA would differ somewhat from the polymer derived from PPDA either in crystallinity or in orientation. Since, in the present work one of the most important problems concerns the solubility or fusibility of the polymer during the polymerization process, it was decided to evaluate m-phenylenediamine and some of its derivatives in the synthesis of this class of polymeric Schiff bases.

The polymerizations of xylylidenetetraethyl ether with m-phenylenediamine were performed without and with benzalaniline and compared in a number of cases with p-phenylenediamine. The results are summarized in Tables 31 and 32.

Table 31

Reaction of MPDA and XTE in the Absence of BA

Exper. No.	Reaction Condition °C/mm Hg Pressure : Hours	Polymer Yield %	Appearance of Polymer
DA-26-274	100/760 : 1.5	108	almost black with dark-brown areas
	170-230/760 : 17.5		
	230/0.5 : 10.0		
DA-26-275	100/760 : 1.5	254	black
	170-230/760 : 17.5		
	230/0.5 : 10.0		

Table 32

## Reaction of XTE with Diamines in Presence of BA

Exper. No.	Reaction Condition °C/mm Hg Pressure : Hours	Observation in Each Stage	Appearance and Yield %
DA-26-279 $p\text{-H}_2\text{NC}_6\text{H}_4\text{NH}_2$	90/760 : 1 100/760 : 18 230/0.5 : 7 300/0.1 : 18	Solidified after melting	yellow yellow yellow 150
DA-26-280 $m\text{-H}_2\text{NC}_6\text{H}_4\text{NH}_2$	90/760 : 1 100/760 : 18 230/0.5 : 7 300/0.1 : 18	Viscous solution Very viscous Rubber-like solid Solidified (black)	yellow brown-red red 205
DA-26-281 $p\text{-H}_2\text{NC}_6\text{H}_4\text{NH}_2$	100-110/760 : 6 240-330/1.5→1.0 : 23 440/1.0 : 24	Solidified after melting	dark-brown 156
DA-26-282 $m\text{-H}_2\text{NC}_6\text{H}_4\text{NH}_2$	100-110/760 : 2 100-110/760 : 4 240/1.5 : 7 330/1.0 : 16 440/1.0 : 24	Viscous solution Very viscous Almost solidified Solid Solidified (black)	reddish-brown red black black 173

1. Experimental.a. (DA-26-274) Reaction of MPDA and XTE.

A mixture of 1.4 g. of MPDA and 3.92 g. of XTE were polymerized under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
100	760	1.5	Initially homogeneous
170	760	1.5	Brown solid
180	760	2.5	Brown solid
230	760	13.5	Brown solid
230	0.5	10.0	Almost black, some brown

During the reaction 0.8 g. of distillate was collected and the weight of the polymer was 3.0 g. (108%).

b. (DA-26-275) Reaction of MPDA and XTE in BA.

A mixture of 1.11 g. MPDA, 3.11 g. of XTE and 5 g. of BA was polymerized under the following conditions:

Temp. °C	Pressure mm Hg	Hours	OBservations
100	760	1.5	Viscous orange solution
110	760	4.0	Very viscous, dark orange
180	760	0.5	Reddish brown; little viscous flow
180	760	12.0	Dark-brown, no flow
230	0.5	24.0	Black, hard solid

During the reaction 2.3 g. of distillate was collected. Yield of black polymer was 5.6 g. (254%).

c. (DA-26-279) Reaction of PPDA and XTE in BA.

A mixture of 1.192 g. of PPDA, 3.240 g. of XTE and 5 g. of BA was polymerized under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
90	760	1.0	Initial melt; yellow solid
100	760	18.0	Orange solid
230	0.5	17.0	Brown solid
300	0.1	18.0	Brown solid

During the reaction 2.6 g. of distillate was collected and the weight of brown polymer was 3.6 g. (150%).

d. (DA-26-280) Reaction of MPDA and XTE in BA.

A mixture of 1.010 g. of MPDA, 2.72 g. of XTE and 5 g. of BA was polymerized under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
90	760	0.5	Yellow fluid melt
90	760	0.5	Viscous, dark yellow
100	3.5	3.5	Very viscous; brown
100	13.0	14.0	Rubbery; reddish brown
230	7.0	7.0	Hard; very dark red
300	0.1	18.0	Hard; black.

During the polymerization 2.2 g. of distillate was collected and the yield of black polymer was 3.8 g. (200%).

e. (DA-26-281) Reaction of PPDA and XTE in BA.

A mixture of 1.446 g. of PPDA, 3.92 g. of XTE and 5 g. of BA were polymerized under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
100	760	6.0	Initial melt; yellow solid
240	1.5	7.0	Dark yellow solid
300	1.0	16.0	Yellow brown solid
400	1.0	24.0	Dark brown solid

The yield of dark brown polymer was 4.5 g. (156%).

f. (DA-26-282) Reaction of MPDA and XTE in BA.

A mixture of 1.422 g. of MPDA, 3.820 g. of XTE and 5 g. of BA were polymerized under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
100	760	6.0	Red, viscous fluid
240	1.5	7.0	Dark red almost solid
330	1.0	16.0	Dark brown solid
440	1.0	24.0	Black solid



The yield of black polymer was 4.9 g. (173%).

## 2. Discussion.

The difference in the behavior of m-phenylenediamine and p-phenylenediamine when subjected to polymerization with p-xylylidenetetramethyl ether is very marked. In the absence of benzalaniline, the polymer obtained with MPDA is dark-brown, almost black, compared to the yellowish polymer obtained when PPDA is used. The yield with MPDA is slightly higher than 100%, whereas with PPDA the yield is still much higher. The difference is due to the fact that the system based on MPDA remains fluid much longer allowing propagation to occur to a higher conversion. However, in both cases, conversion to the black polymer is facilitated by the use of BA as a solvent, but due to incomplete elimination of BA as a result of telomerization by BA, an increase in yield over theory is observed. It was also noted that the polymers prepared in the presence of BA could be heated at temperatures as high as 440°C (DA-26-281 and DA-26-282), yet there was no marked evidence of liberation of BA or of decomposition. This would indicate that the polymers had been telomerized by BA and that the chain ends were frozen in a medium of associated polymer chains of extremely high viscosity, thereby retarding chain-end coupling.

### H. Polymerization of Xylylidenetetraethyl Ether with Dibenzylidene-m-phenylenediamine in Benzalaniline.

The polymerization of dibenzylidene-m-phenylenediamine (DBMPD) and XTE was performed in the presence of BA and compared to one performed without BA. The results are shown in Table 33.

Table 33

## Yields in Polymerization of DBMPD and XTE

Exper. No.	BA	Yield %	Appearance of Polymer
DA-26-283	present	148	black
DA-26-284	present	155	black
DA-26-286	absent	107	black

1. Experimental.a. (DA-26-283) Reaction of DBMPD and XTE in BA.

A mixture of 1.7 g. of DBMPD, 1.818 g. of XTE and 5 g. of BA was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
170-180	15.0	2	yellow-to-brown solution
200	15.0	1	brown solution
230	15.0	6	dark brown, viscous
340-350	0.5	19	black solid

The yield of black polymer was 1.85 g. (148%).

b. (DA-26-284) Reaction of DBMPD and XTE in BA.

A mixture of 1.5 g. of DBMPD, 1.5 g. of XTE and 5 g. of BA was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
180	15.0	2.0	brown solution
205	15.0	1.0	dark brown, viscous
230	15.0	2.5	very viscous
250	15.0	13.0	almost solid
270	0.2	27.0	black solid

The yield of black polymer was 1.66 g. (155%).

c. (DA-26-286) Reaction of DBMPD and XTE.

A mixture of 1.39 g. of DBMPD and 1.399 g. of XTE was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
180-190	15.0	2	dark-brown solution, not viscous
230	15.0	4	solid, dark
250	0.2	13	almost black solid
270	0.2	27	black solid

The yield of polymer was 1.1 g. (107%) of a porous, brittle black polymer.

2. Discussion.

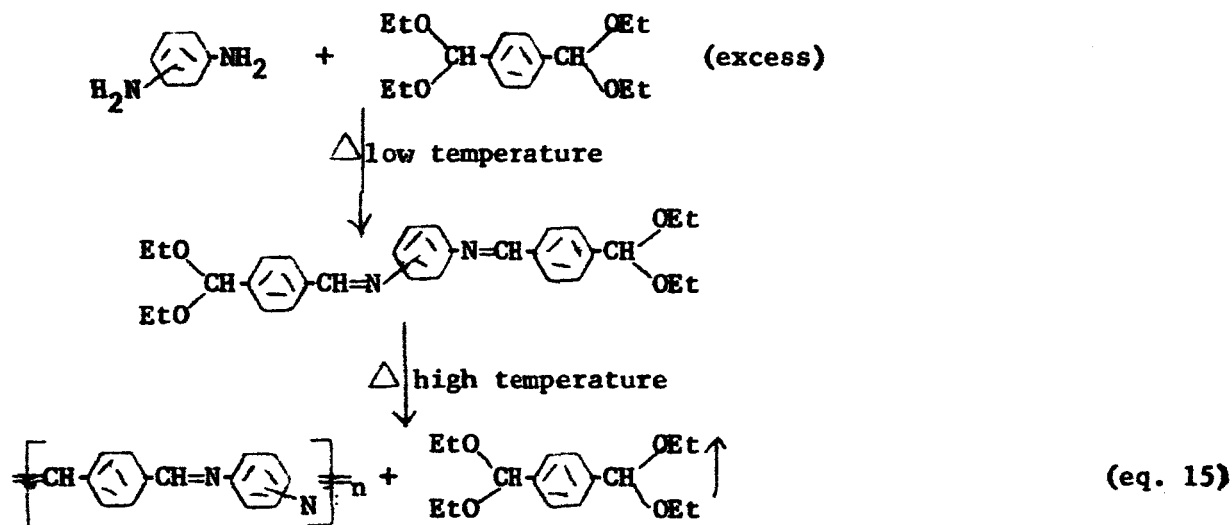
The data of Table 33 indicates that benzalaniline is retained in the polymer, some of it probably as a result of telomerization, and the remainder in solution in the polymer. Though a black polymer is obtained in the reaction of DBMPD and XTE in its absence, the black polymer is not readily fusible and is friable. Nonetheless, the great difference in the behavior of the meta and the para dibenzylidene derivatives is observable as it was in their parent diamines. The better fusibility and solubility of the meta compounds allows the reaction to proceed more readily to the black polymer stage.

In the case of p-phenylenediamine, in the absence of BA, the oligomers which are formed in the early stage of reactions are very insoluble and infusible in the reaction mass so that propagation of the chain is inhibited. For this reason only yellow products are obtained in this reaction system. However, the oligomers obtained in the polymerization of xylylidenetetraethyl ether with m-phenylenediamine have zig-zag type of configuration which gives the oligomer greater solubility and fusibility. These properties make possible the further propagation of the oligomer to a higher molecular weight and color of the polymer changes from yellow to darker colors. In this system,

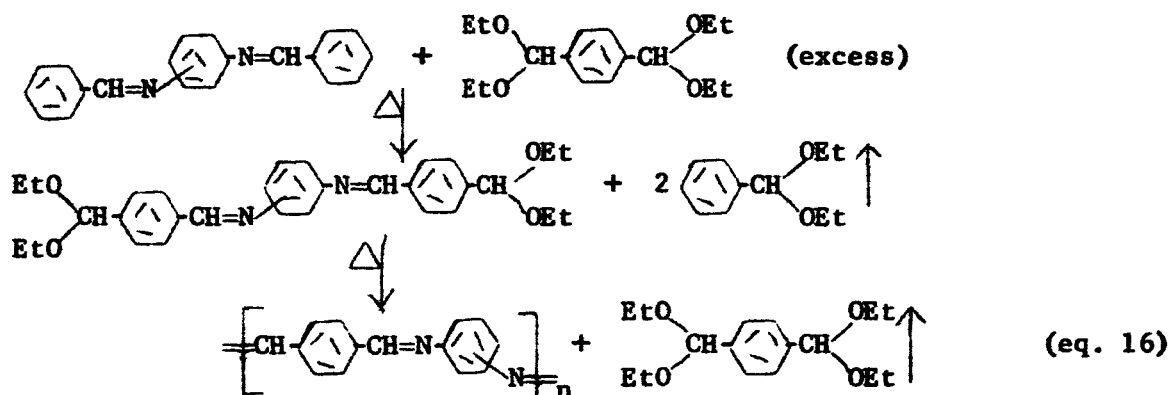
dark-brown, almost black, polymers are obtained almost quantitatively. In contrast, in the polymerization of DBMPD with XTE the yields are always over 100% but are much lower than when DBPPDA is used as a starting material.

I. Polymerization of Phenylenediamines or Dibenzylidene-phenylenediamines in an Excess of Xylylidenetetraethyl Ether.

The types of polymerizations given in equations 15 and 16 were studied:



and



The purpose of these studies then is to evaluate the use of xylylidenetetraethyl ether as a solvent instead of benzalaniline. It was hoped that the solubility of the intermediate oligomers would be increased by having both ends telomerized by xylylidenetetraethyl ether. The studies were performed using p- and m-phenylenediamine, and p- and m-dibenzylidenephenylenediamine as the amine reagent with XTE. The results are summarized in Table 34.

Table 34

## Polymerizations With Excess of Xylylidenetetraethyl Ether

Expt. No.	Excess Acetal Mole %	Yield %	Appearance of Polymer
DA-26-290 p-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	200	101	black partially dark-brown
DA-26-291 m-H <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	200	115	black
DA-26-293 Dibenzylidene-p-phenylenediamine	100	58	black
DA-26-294 Dibenzylidene-m-phenylenediamine	100	50	black
DA-26-295 Dibenzylidene-p-phenylenediamine	100	143	black
DA-26-206 Dibenzylidene-m-phenylenediamine	100	163	black

1. Experimental.a. (DA-26-290) Reaction of PPDA and XTE.

A mixture of 0.99 g. of PPDA and 8.1 g. of XTE (1:3 mole ratio) was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
140	760	3.5	yellow solid
180	1	1.0	yellow solid
330	0.6	15.0	brown solid
370	0.6	5.0	black and brown solids

During the course of the reaction 4.6 g. of XTE were recovered as distillate; and the weight of the polymer was 2.0 g. (101%).

**b. (DA-26-291) Reaction of MPDA and XTE.**

A mixture of 1.040 g. of MPDA and 8.1 g. of XTE (1:3 mole ratio) was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
140	760	1.0	yellow solid and liquid
140	1	2.5	viscous with yellow solid
180	1	1.0	dark-brown-orange solid
330	0.6	15.0	black solid

During the course of the reaction 2.9 g. of XTE were recovered and the yield of polymer was 2.4 g. (115%).

**c. (DA-26-293) Reaction of DBPPDA and XTE.**

A mixture of 1.011 g. of DBPPDA and 2.022 g. of XTE (1:2 mole ratio) was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
180-200	20.0	2	thin yellow solution
240	10	19	brown viscous solution
300	0.4	12	very viscous dark-brown
400	0.4	12	black solid

During the reaction 1.7 g. of liquid distillate ( $C_2H_5OH$  and XTE) as well as 0.5 g. of DBPPDA were recovered. The yield of black polymer was 0.45 g. (68%) due to incomplete reaction of DBPPDA.

**d. (DA-26-294) Reaction of DBMPD and XTE.**

A mixture of 1.122 g. of DBMPD and 2.244 g. of XTE (1:2 mole ratio) was

reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
180-200	20.0	2	thin brown solution
240	10.0	19	dark brown, viscous
300	0.4	12	black solid

During the reaction 1.45 g. of liquid distillate of alcohol and XTE were recovered. Also recovered were 0.4 g. of DBMPD. The yield of black polymer was 0.5 g. (60%).

e. (DA-26-295) Reaction of DBPPDA and XTE.

A mixture of 2 g. of DBPPDA and 4 g. of XTE (1:2 mole ratio) was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
220-240	200	2.5	dark-brown solution
220-240	100	3.5	viscous, dark-brown
280	1.0	7.0	solid brown-black
360	1.0	48.0	black solid
400	1.0	14.0	black solid

During the reaction 1.3 g. BDE and 0.8 g. XTE were recovered and the yield of polymer was 2.1 g. (143%).

f. (DA-26-296) Reaction of DBMPD and XTE.

A mixture of 2 g. of DBMPD and 4 g. of XTE was reacted under conditions identical to those given in DA-26-295. The polymer obtained was black and amounted to 2.4 g. (163%).

2. Discussion.

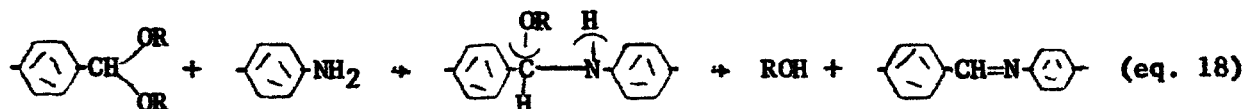
The following conclusions may be drawn from the above results. The polymerization of p-phenylenediamine with excess amount of xylylidene-tetra-ethyl ether produced dark brown-black polymer with approximately 100% yield.

During the first stage of the low reaction temperature, 91% of theoretical amount of alcohol was recovered, and in the further stages, at the higher reaction temperature, 85% of theoretical excess of xylylidenetetraethyl ether was recovered, indicating that this reaction proceeds in the manner indicated in equation 15.

In the case of the reaction using m-phenylenediamine with XTE in excess, the polymer was produced in a yield in excess of 100%; this is in contrast to an equimolar polymerization reaction and is attributable to the low reactivity of the meta-substituted oligomers. This observation was also confirmed in the difference in yield between dibenzylidene-p-phenylenediamine and dibenzylidene-m-phenylenediamine.

J. Polymerization of Xylylidenetetra-n-butyl Ether with p-Phenylenediamine or its Derivatives.

In the polymerizations of diacetals and diamines and their derivatives, it was considered<sup>1</sup> that reactions proceeded through an intermediate state from which the alcohol was eliminated. When the intermediate is soluble or fusible, propagation of the chain proceeds to a high degree since it will not be retarded by precipitation from the medium; then the intermediate will convert to a Schiff base polymer of high molecular weight. Too, the molecular weight of a polymer depends on the stability of the intermediate as well as on its solubility and fusibility. On this basis, it was decided to evaluate a different alkyl group in the acetal. In the following reaction, one would expect that stability of the intermediate would increase with the size of R:



For this evaluation, xylylidenetetra-n-butyl ether (DA-26-259) (XTBE) was chosen for comparison with the tetraethyl ether (XTE)



**1. Polymerization of Xylylidenetetra-n-butyl Ether with p-Phenylenediamine.**

The results obtained in these studies are shown in Table 35.

Table 35

Polymerization of XTBE with PPDA.

Exper. No.	Solvent	Yield %	Appearance of Polymer
DA-26-261	Bulk	93	brown
DA-26-262	DMA	93	brown
DA-26-263	DMF	111	yellow
DA-26-264	Bulk	104	yellow
DA-26-266	Benzalaniline 20 wt. %	86	yellow
DA-26-267	Benzalaniline 50 wt. %	94	yellow

**a. Experimental.**

**i. (DA-26-259) Synthesis of Xylylidenetetra-n-butyl Ether.**

A mixture of 30 g. TA, 150 g. n-C<sub>4</sub>H<sub>9</sub>OH, 2 g. p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H and 200 ml. benzene was heated at reflux in a Dean-Stark apparatus and the water formed by the reaction was collected in the trap. The reaction was continued for eleven hours and the amount of water separated was 7.9 ml. (99% of theory). Then, after neutralizing the reaction mixture with aqueous Na<sub>2</sub>CO<sub>3</sub>, the product was dried over anhydrous Na<sub>2</sub>CO<sub>3</sub> and fractionally distilled. The fraction boiling at 163°C at 0.4 mm Hg pressure (84%) was collected and its IR spectrum recorded.

**ii. (DA-26-261) Reaction of PPDA and XTBE.**

A mixture of 1.212 g. of PPDA and 3.636 g. of XTBE was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
160	760	1	thin yellow melt
160	15	3	yellow solid
220	15	5	dark yellow solid
250	15	40	brown solid

The yield of polymer was 1.6 g. (93%).

iii. (DA-26-262) Reaction of PPDA and XTBE in Dimethylacetamide (DMA).

A mixture of 1.370 g. PPDA, 4.104 g. of XTBE and 6 g. of DMA was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
40-60	760	1	yellow solution
160	760	4	yellow solid
200-220	760	5	dark yellow, solid
250	760	40	brown solid

The yield of polymer was 2.4 g. (93%).

iv. (DA-26-263) Reaction of PPDA and XTBE in Dimethylformamide (DMF).

A mixture of 1.166 g. of PPDA, 4.660 g. of XTBE and 10 g. of DMF was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
160-200	760	2.5	yellow solution
200	760	0.5	yellow precipitate
230	760	20.0	yellow solid

The yield of polymer was 2.6 g. (111%) and about 90% of the theoretical amount of butyl alcohol was collected during the reaction.

v. (DA-26-264) Reaction of PPDA and XTBE.

A mixture of 1.247 g. of PPDA and 4.988 g. of XTBE was reacted under

the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
160-200	760	2	yellow solution
230	760	20	yellow solid

The yield of yellow polymer was 2.6 g. (104%) and 80% of the theoretical amount of butyl alcohol was collected during the reaction.

vi. (DA-26-266) Reaction of PPDA and XTBE in BA.

A mixture of 0.906 g. of PPDA, 3.618 g. of XTBE and 1.0 g. of BA was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
200-210	15.0	0.7	yellow solution
220	15.0	4.0	yellow precipitate
250	0.8	20.0	yellow solid

The yield of yellow polymer was 1.55 g. (86%).

vii. (DA-26-267) Reaction of PPDA and XTBE in BA.

A mixture of 1.125 g. PPDA, 4.500 g. of XTBE and 5 g. of BA was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
220	760	0.1	yellow solution
220	760	4.9	yellow precipitate
250	20	12.0	yellow solid
310	0.5	72.0	yellow solid

The yield of yellow polymer was 2.1 g. (94%).

b. Discussion.

In every case, the reactivity of xylylidenetetra-n-butyl ether was

remarkably low and reaction did not occur below 150°C. However, on increasing the reaction temperature to about 160°C, a reaction was observed after about one hour of heating. The yield of polymers in all cases was almost theoretical. It is surprising the yield was not over 100% even in those polymerizations performed in the presence of benzalaniline. Unexpectedly, all products are yellow. The low yield in DA-26-266 was due probably to loss of low molecular weight products by distillation during the reaction. The low reactivity of XTBE can also be attributed to steric factors.

## 2. Polymerization of Xylylidenetetra-n-butyl Ether with Dibenzylidene-p-phenylenediamine.

The results obtained in these studies are summarized in Table 36

Table 36

Reaction of DBPPDA and XTBE

Exper. No.	Solvent	Catalyst	Polymer Yield %	Appearance of Product
DA-26-268	Bulk	None	0	no reaction
DA-26-270	BA	None	0	no reaction
DA-26-272	DMA	Yes	100	brown-black polymer

### a. Experimental.

#### i. (DA-26-268) Reaction of DBPPDA and XTBE.

A mixture of 1.81 g. of DBPPDA and 2.53 g. of XTBE was reacted at 200°C at 15 mm Hg pressure for three hours, and at 240°C at 15 mm Hg pressure for twenty-four hours. Reaction did not occur and the reactants were recovered.

#### ii. (DA-26-270) Reaction of DBPPDA and XTBE in BA.

A mixture of 1.25 g. of DBPPDA, 1.86 g. of XTBE and 5 g. of BA was reacted at 220°C at 760 mm Hg pressure for four hours, then at 220°C at 15 mm Hg pressure for twelve hours, followed by 240°C at 15 mm Hg pressure for three hours. Reaction failed to occur and the reagents were recovered.

iii. (DA-26-272) The Catalyzed Reaction of DBPPDA, XTBE and BA.

A mixture of 1.50 g. of DBPPDA, 2.31 g. of XTBE, 20 g. of DMA and 0.1 g. of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$  was reacted at  $280^\circ\text{C}$  at 15 mm Hg pressure for twelve and one-half hours. The mixture became black and as the DMA distilled out, the solution became very viscous and finally solid. Yield of black polymer was 1.1 g. (100%).

b. Discussion.

The polymerization of XTBE with DBPPDA does not occur without a catalyst even at  $240^\circ\text{C}$ ; however, by using a catalyst the reaction proceeds quantitatively and black polymer products are obtained.

3. Polymerization of p-Xylylidenetetra-n-butyl Ether with Di-N-Acyl-p-phenylenediamine (DAPD).

The results of these studies are shown in Table 37.

Table 37

Polymerization of XTBE and DAPD

Exper. No.	Solvent	Catalyst	Polymer Yield %	Appearance of Polymer
DA-26-271	BA	none	0	-----
DA-26-269	DMA	none	0	-----
DA-26-273	DMA	yes	106	black

a. Experimental.

1. (DA-26-271) Reaction of DAPD and XTBE in BA.

A mixture of 3.02 g. of DAPD, 1.13 g. of XTBE and 5 g. of BA was reacted at  $220^\circ\text{C}$  at 760 mm Hg pressure for sixteen hours; at  $240^\circ\text{C}$  at 760 mm Hg pressure for four hours, then at  $240^\circ\text{C}$  at 15 mm Hg pressure for eleven hours. Reaction did not occur and the reagents were recovered.

ii. (DA-26-269) Reaction of DAPD and XTBE in DMA.

This reaction is identical to DA-26-271 except that dimethylacetamide

was used instead of benzalaniline.  
occurred.

In this case also no reaction

iii. (DA-26-273) Catalyzed Reaction of DAPD and XTBE in DMA.

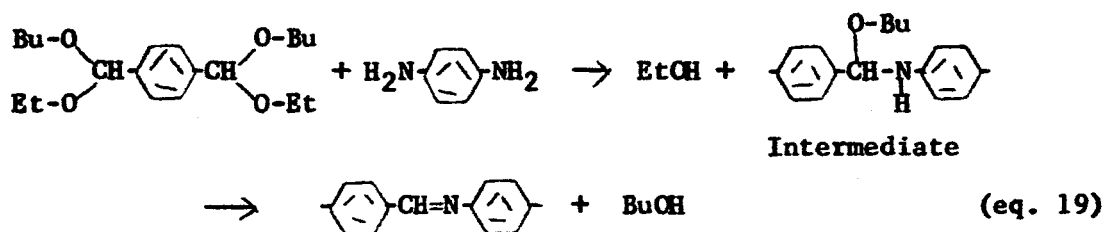
A mixture of 1.13 g. of DAPD, 3.10 g. of XTBE, 10 g. of DMA and 0.2 g. of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$  was reacted at  $200^\circ\text{C}$  at 760 mm Hg pressure for twenty-three hours, and at  $280^\circ\text{C}$  at 15 mm Hg pressure for eighteen hours, yielding 1.3 g. (106%) of a black solid polymer.

b. Discussion.

The reaction of XTBE with DAPD in the absence of a catalyst does not proceed. However, it can be catalyzed by *p*-toluene sulfonic acid, then black polymers are produced in almost quantitative yields.

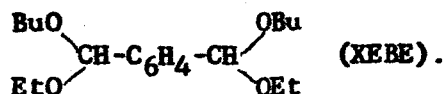
K. Preliminary Evaluation of a Mixed Acetal and its Polymerization Reaction with Diamine.

In Section J, the reactivities of xylidenetetra-*n*-butyl ether to amine and amine derivatives were shown to be very low. It was hoped that a mixed diacetal, that is, one containing the relatively unreactive butyl group along with a more reactive alkyl group, such as the ethyl group, would yield a high molecular weight fusible intermediate, which then, on heating, would be converted to a high molecular weight Schiff base polymer. For example, the polymerization reaction between the mixed ethyl-butyl-diacetal and the diamine would proceed as shown in equation 19:



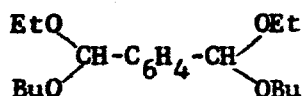
1. Synthesis of a Mixed Diacetal.

The procedure<sup>19</sup> given by Alquier was used to synthesize



a. (DA-26-276) Synthesis of a Mixed Acetal.

Xylylidenetetraethyl ether (XTE) 14 g. and 10 g. of xylylidenetetra-n-butyl ether (XTBE) in 150 ml. of benzene containing 0.4 g. of p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H were refluxed for twenty hours and the product fractionally distilled. The fraction (13 g.) boiling at 142-148°C at 0.2 mm reduced pressure was collected. This fraction appeared to be a mixture of (EtO)<sub>2</sub>CHC<sub>6</sub>H<sub>4</sub>CH(OBu)<sub>2</sub> and



The mixture was used in the polymerization as compound

XEBE.

2. Polymerization of a Mixed Acetal with p-Phenylenediamine.

The conditions and results are shown in Table 38.

Table 38

Reaction of PPDA and XEBE

Exper. No.	Reaction Condition °C/mm Hg : Hours	Yield %	Appearance
DA-26-278	180/760 mm Hg : 3 240/760 mm Hg : 14	98	yellow

a. Experimental.

1. (DA-26-278) Reaction of PPDA and XEBE.

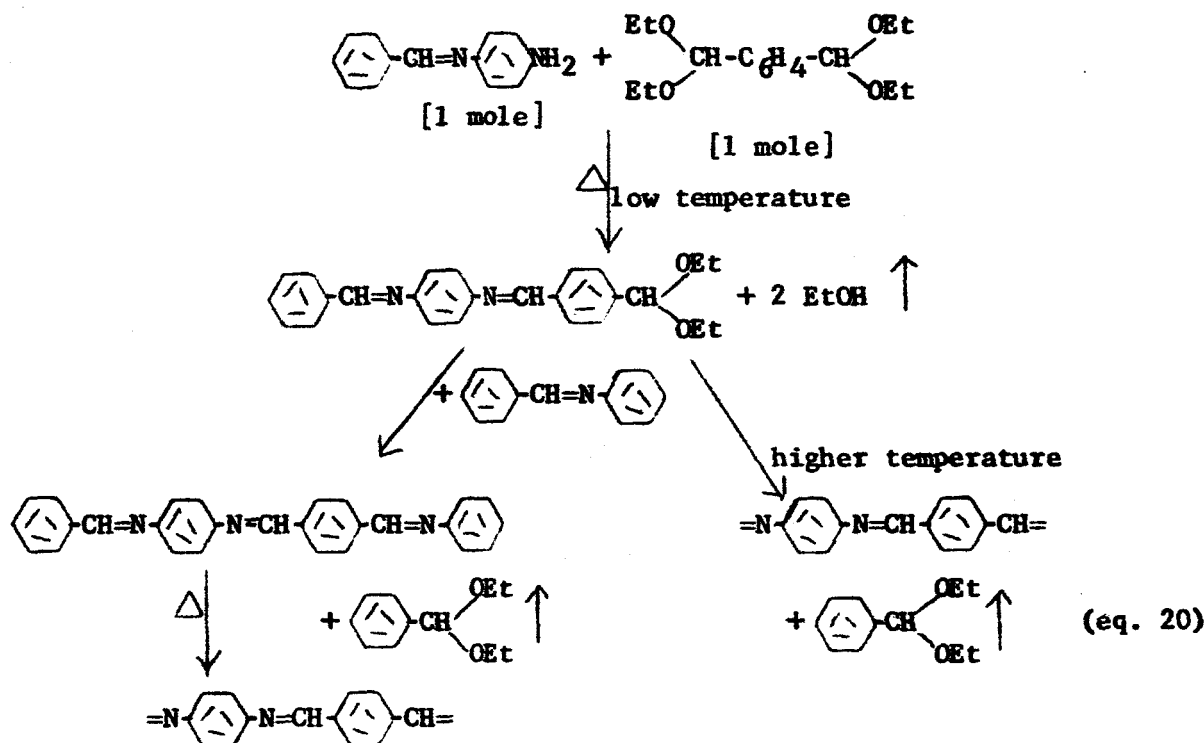
A mixture of 1.112 g. of PPDA and 3.65 g. of XEBE was reacted at 180°C at 760 mm Hg pressure for three hours; then at 240°C at 760 mm Hg pressure for fourteen hours. Both ethanol and butanol were collected in the distillate. The polymerization occurred readily at 180°C, and the yellow polymer precipitated without passing through a viscous stage. Yield of yellow powdery polymer was 2.3 g. (104%).

### b. Discussion.

In this experiment, the purity of the mixed acetal was doubtful, that no conclusion can be drawn as to whether or not the mixed acetal technique is superior to the use of a standard acetal.

#### L. Polymerization of Xylylidenetetraalkyl Ether with Monobenzalphenylenediamine (MBPD).

The polymerization reactions given by equation 20 were studied:

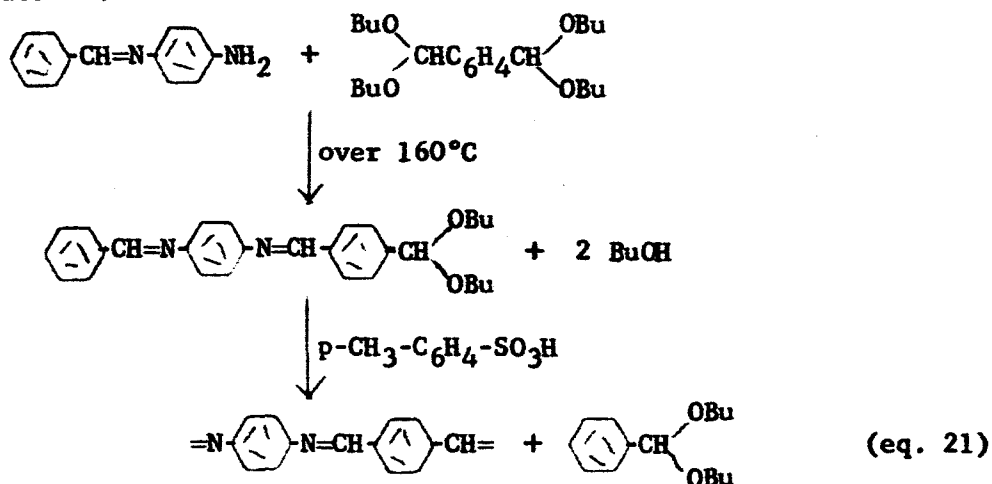


The reaction scheme in equation 20 is, of course, idealized, since, in the first stage of this reaction there is a high probability that in addition

to the formation of  $\text{C}_6\text{H}_5\text{-CH=N-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_4\text{-CH(OEt)-OEt}$ , some  $\text{C}_6\text{H}_5\text{-CH=N-C}_6\text{H}_4\text{-N=CH-C}_6\text{H}_4\text{-CH=N-C}_6\text{H}_4\text{-NH}_2$  will also form, leaving unreacted  $\text{EtO-CH(C}_6\text{H}_4\text{)-CH(OEt)-C}_6\text{H}_4\text{-CH(OEt)-OEt}$ . If a large excess of  $\text{EtO-CH(C}_6\text{H}_4\text{)-CH(OEt)-C}_6\text{H}_4\text{-CH(OEt)-OEt}$  is used, this probability would be diminished. Accordingly, equimolar reactions and reactions with excess amounts of xylylidenetetraethyl ether were performed.



Both xylylidenetetra-*n*-butyl ether and xylylidenetetraethyl ether were used. Because of the reduced reactivity of the tetra-butyl ether, it should be possible to achieve the reactions given by equation 21 by controlling the reaction conditions.



The results of these studies are summarized in Table 39.

Table 39

Reactions of MBPD and XTE or XTBE

Exper. No.	Atetal	Ratio of Acetal to Schiff Base or Amine	Solvent	Catalyst	Yield %	Appearance
DA-26-299	Et	1	none	none	103	dark brown
DA-26-300	Et	1	DMF	none	98	dark brown
DA-26-301	Et	1	none	none	97	brown-black
DA-26-302	Et	1	DMF	none	99	black
DA-26-305 with C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	Et	1	none	none	120	black
DA-26-306 with C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>5</sub>	Et	1	DMF	none	125	black
DA-26-307	Et	3	none	none	95	black
DA-26-308	Bu	1	DMF	none	95	black

## 1. Experimental.

### a. (DA-26-292) Synthesis of Monobenzal-p-phenylenediamine (MBPD).

A mixture of 320 ml. of alcohol and 20 g. of p-phenylenediamine was placed in a flask equipped with a stirrer and a reflux condenser, and the mixture heated at 50°C. When the diamine was dissolved in the alcohol, 15 g. of benzaldehyde was added dropwise over a period of three hours with continuous stirring. Then the alcohol was removed by evaporation in a flash evaporator at room temperature. Then 100 ml. of benzene was added and an insoluble fraction was removed by filtration; it amounted to 5.0 g., m.p. 138°C, and was identified by its IR spectrum as p-phenylenediamine. The benzene filtrate was concentrated in a flash evaporator, and the solid product was recrystallized twice from 50 ml. of ethyl ether. The yield of yellow product, m.p. 63-65°C amounting to 22 g. is very soluble in alcohol, benzene and ether, and is insoluble in n-hexane. Its IR spectrum was recorded.

### b. (DA-26-299) Reaction of MBPD and XTE.

A mixture of 2.09 g. of MBPD and 3.02 g. of XTE was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
150	300	5.5	partial melt; yellow solid
230	150	12.0	brown solid
340	1	20.0	dark brown solid

The yield of polymer was 2.3 g. (103%).

### c. (DA-26-300) Reaction of MBPD and XTE in DMF.

A mixture of 1.348 g. of MBPD, 1.940 g. of XTE and 10 g. of DMF was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
150	760	5.5	yellow precipitate
230	150	12.0	brown solid
340	1	20.0	brown-black solid

The yield of polymer was 1.4 g. (98%).

d. (DA-26-301) Reaction of MBPD and XTE.

A mixture of 1.000 g. of MBPD and 1.501 g. of XTE was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
150	10	3	yellow-brown solid
360-400	1	24	brown-black solid

The yield of polymer was 1.03 g. (97%).

e. (DA-26-302) Reaction of MBPD and XTE in DMF.

A mixture of 1.0 g. of MBPD, 1.5 g. of XTE and 5.0 g. of DMF was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
180	760	6	yellow solid
360-400	1	24	black solid

The yield of polymer was 1.05 g. (99%).

f. (DA-26-305) Reaction of MBPD and XTE in BA.

A mixture of 1.095 g. of MBPD, 1.580 g. of XTE and 1.0 g. of BA was heated at 760 mm Hg pressure at 180°C and raised over the period of thirteen hours to 270°C, followed by heating for twenty hours at 760 mm Hg pressure at 270-290°C, and then heated at 330°C at 0.2 mm Hg pressure for

seven hours. The yield was 1.49 g. (120%) of black polymer.

g. (DA-26-306) Reaction of MBPD and XTE in BA and DMF.

A mixture of 1.083 g. of MBPD, 1.56 g. of XTE, 1 g. of BA and 10 g. of DMF was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
150-180	760	6.0	yellow solution and solid
245	760	19.5	brown solid
330	0.7	13.5	black solid

The yield of polymer was 1.5 g. (125%).

h. (DA-26-307) Reaction of MBPD with Excess XTE.

A mixture of 2.315 g. of MBPD and 10.50 g. of XTE was reacted under the following conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
60-80	760	4.0	brown solution
130	760	0.5	brown solid
180	0.3	3.0	dark brown solid
290	0.3	12.0	brown-black solid
330	0.3	2.0	black solid
360	0.3	12.0	black solid

The yield of polymer was 2.3 g. (95%).

i. (DA-26-308) Catalyzed Reaction of MBPD with XTBE.

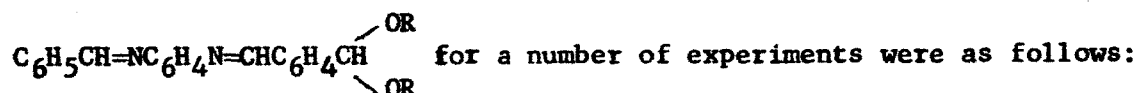
A mixture of 0.952 g. of MBPD and 1.95 g. of XTBE was reacted for two hours under the conditions given below; then 0.1 g. of  $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$  in 99% DMF added after the theoretical amount of butyl alcohol was collected and the polymerization continued under the indicated conditions:

Temp. °C	Pressure mm Hg	Hours	Observations
160-180	760	0.5	yellow melt
180	10	0.5	yellow solid 98% BuOH recovered catalyst added
200	760	2.0	brown melt
400	0.3	12.0	black solid

The yield of polymer was 0.97 g. (95%).

## 2. Discussion.

The yield of alcohol based on the formation of the intermediate,



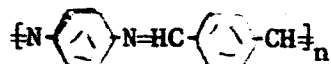
Exper. No.	Yield %	Kind of Alcohol
DA-26-299	96	ethanol
DA-26-307	108	ethanol
DA-26-308	98	n-butanol

In most cases the polymers were black, and yields were in the range of theoretical values. However, the yield, in those cases in which BA was used, were over 100%.

## V. Post Reactions of Polymers.

### A. Post Reactions Leading to an Increase in the Degree of Polymerization.

Schiff base polymers having the conjugated structure



would be expected to show a shift in color from yellow to black with increasing value of  $n$ . A general shift in color is indeed observed for many polymers produced by Schiff base exchange reactions. Some polymers, particularly those obtained by condensation or melt polymerizations, have been found to be yellow or brown. It is desirable, therefore, to find a method by which these oligomers could be polymerized further to black, high molecular weight polymers.

Two techniques were employed to increase the molecular weight of these polymers. First, the polymers were heat-treated to cause polymerization in the solid state. Reactive end groups would be expected to become more mobile at higher temperatures, and further condensation should occur between chain ends. The second method involves preparing solutions of such low molecular weight polymers in BA followed by heating to extend the reaction in a homogeneous system. It had been observed that melt-solution polymerization using BA very often gave high molecular weight polymers which were black. On this basis, BA was added to low molecular weight polymers with the expectation of polymerizing them to the black stage.

#### 1. Experimental.

##### a. (DA-26-151) Post Heating of Polymer DA-29-121 Obtained by Melt-Solution Polymerization.

One gram of the fusible black polymer was ground to a fine powder and placed in a 50 ml. round-bottomed flask. The polymer was heated under nitrogen by means of a metal bath to 420°C for forty-five hours at 1.5 mm Hg

pressure. A yellow-brown residue was found on the surfaces of the distilling head and the condenser when the reaction was terminated. The weight of polymer had decreased to 0.64 g. Projecting this weight loss over the original yield in DA-29-121 gives a final yield of 92%, whereas before treatment the yield had been 114%.

b. (DA-29-126) Post Heating of Condensation Polymer DA-29-94 in BA.

Two grams of the yellow brick dust condensation polymer DA-29-94 was mixed with 4 g. of BA and heated in a polymerization apparatus under the conditions listed in Table 40.

Table 40

Time (hours)	Temp. °C	Pressure
2	140	atm
2	200	atm
4	260	atm
10	320	atm
10	300	140 mm
10	300	1 mm

After reaction, the polymer was reexamined and found to be black and shiny, which had foamed considerably. An ammonia-like gas was observed in the collection trap. Further heating at bunsen flame temperatures melted the polymer, and this was followed by foaming of the polymer. The black polymer, due to incorporation of some BA, weighed 4.27 g.

c. (DA-29-127) Repeat of DA-29-126 Using Somewhat Different Conditions.

The same amounts of polymer and BA were used as in DA-29-126. The conditions, however, were changed and are shown in Table 41.

Table 41

Time (hours)	Temp. °C	Pressure
5	250	atm
18	290	atm
10	340	atm
14	340	140 mm

At the end of the reaction there was isolated 3.05 g. of polymer, parts of which were glassy and other parts were foamed and dull. A liquid nitrogen trap was used in the reaction system in an attempt to collect any ammoniacal or other degradation products. No product, other than BA, was found in the trap at the end of the reaction.

d. (DA-29-148) Post-Heating of Amine Exchange Polymer DA-29-132.

One gram of polymer DA-29-132 and 10 g. BA were heated to reflux under nitrogen at 300°C for ten hours. As the reaction progressed, the melt became darker in color with the polymer dissolving until all the solution was black. At this point, the melt appeared to be homogeneous. One quarter gram of zinc chloride was added and heating continued at 300°C for forty-eight hours. The liquid melt solidified to a black solid. The product was removed from the flask and extracted with 95% ethanol for five days. After drying the product, 6.20 g. of a brown polymer, was obtained.

2. Discussion.

By heating polymers with yields in excess of 100% at high temperatures, it is possible to lower the yields to near theoretical values. Heating at high temperatures and long periods of time causes substances incorporated within the mass of polymer to diffuse out and to be removed by volatilization. After prolonged heating, the polymer is usually a jet black color and possesses exceptional toughness.



The addition of BA to low molecular weight polymers solubilizes these materials but also leads to incorporation of some of the BA into the polymer. BA once incorporated into a polymer is held tenaciously and is not easily removed; hence, the yields of polymers obtained are high. The action of BA in these systems cannot be entirely ascribed to its solvent properties. Schiff base exchange may also involve BA.

## B. Attempts to Determine the Solubility of Certain Polymers.

### 1. Experimental.

Two solvents, acetic anhydride and concentrated formic acid were evaluated in attempts to dissolve Schiff base polymers.

#### a. (DA-29-152) Attempted Solution of Condensation Polymer DA-29-94 in Acetic Anhydride.

Yellow polymer DA-29-94, 0.1 g. was refluxed in a round-bottomed flask with 100 ml. acetic anhydride. Refluxing was continued for a period of forty-eight hours. After this time, most of the polymer remained as a precipitate in the bottom of the flask; however, a small amount did go into solution as was evidenced by the pale yellow color of the acetic anhydride.

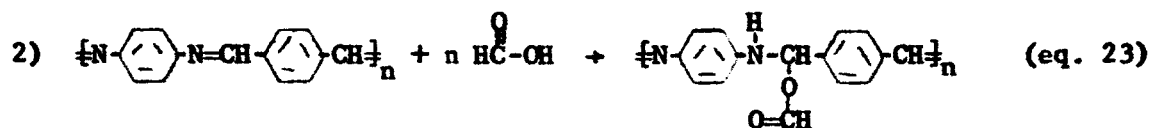
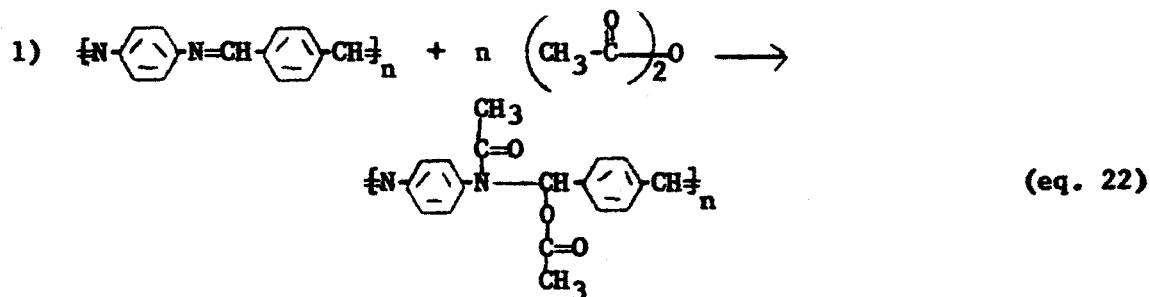
#### b. (DA-29-153) Attempted Solution of Polymer DA-29-67 in Concentrated Formic Acid.

The black polymer DA-29-67 (0.002 g.) obtained by a condensation reaction of TA and PPDA in BA was refluxed with 10 ml. 98+% formic acid for forty-eight hours. A very pale yellow dilute solution was obtained; however, most of the black polymer remained undissolved. One drop of concentrated sulfuric acid was added to the formic acid solution and the reflux continued for two more days. No change in the system was noted after this time, and the experiment was discontinued.

### 2. Discussion.

Originally, it was hoped that Schiff base polymers could be dissolved by

suitable reagents which react with the  $-C=N-$  linkage as in the monomeric compounds. For example, acetic anhydride and formic acid would be expected to react in the manner indicated in equations 22 and 23.

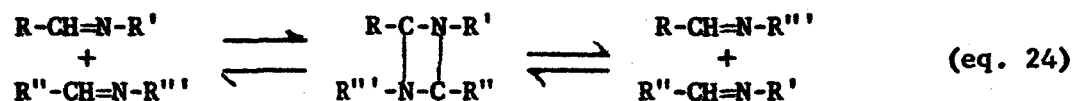


These derivatives, if obtained, should be soluble in organic solvents. Then, molecular weights and other physical data could be obtained from solutions of these polymers. The above experiments indicate, however, that the solubility is very low, if any, and that extraction of impurities or oligomers may actually account for the yellow solutions obtained.

The absence of good solvents for the polymers makes molecular weight determination by the usual methods impossible, and it has been suggested that this problem be the subject of another research project.

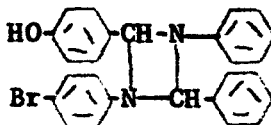
## VI. Mechanistic Considerations and Attempts to Isolate Intermediates.

Mechanisms for the Schiff Base exchange reactions have been proposed.<sup>1</sup> These mechanisms have been postulated to proceed through four-membered ring intermediates. In the bis-Schiff base exchange reaction, the mechanism has been suggested as going through a diazidine intermediate, as shown in equation 24:



To confirm this mechanism, it would be desirable to obtain a system in which the intermediate diazidine could be isolated. One could then demonstrate this intermediacy by decomposing it under the conditions of the normal bis-exchange reaction to give the desired products.

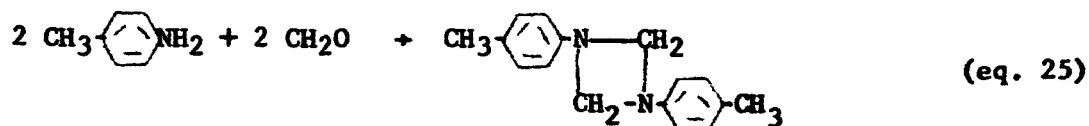
C.K. Ingold and H.A. Piggot described<sup>14</sup> the reaction of p-hydroxybenzylideneaniline and benzylidene-p-bromoaniline to give the unstable diazidine derivative,



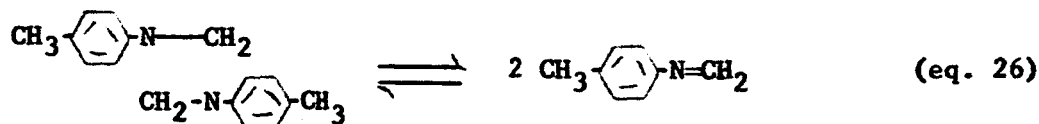
These authors report<sup>14</sup> that the melting

point and chemical characteristics of this compound are considerably different than either of the starting materials.

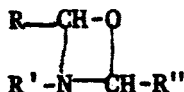
In another paper, Ingold<sup>15</sup> reports the isolation of another more stable diazidine derivative by the reaction of equation 25:



It is stated<sup>15</sup> that the four-membered ring compound is so stabilized over the monomer,  $\text{CH}_3-\text{C}_6\text{H}_4-\text{N}=\text{CH}_2$ , that only at 250°C does the monomeric azomethine exist alone, as shown in equation 26.



Ingold suggests<sup>14,15</sup> that many other exchange type reactions, including the carbonyl exchange, take place by means of four-membered ring intermediates, such as



this type.

The syntheses of the above diazidine derivatives were attempted, both to confirm the work of Ingold and his associates, and to lend further evidence to the proposed mechanism.<sup>1</sup>

#### A. Experimental.

##### 1. (DA-29-164) Reaction of o-Hydroxybenzylidene-aniline and Benzylidene-p-bromoaniline.

Following the procedure of Ingold, 1.22 g. (0.01 mole) p-hydroxybenzylideneaniline was placed in 7 ml. of boiling absolute ethanol. Next, 1.72 g. (0.01 mole) benzylidene-p-bromoaniline was added to the solution. A solution of the two compounds was obtained, after which it was cooled to room temperature. Evaporation of the ethanol under vacuum gave a quantity of yellow-tan crystals. These crystals were removed by filtration and redissolved in 95% cold ethanol. Most of the ethanol was removed by means of a flash evaporator and upon cooling the residue in an ice bath, tan crystals were obtained. This material and the starting material, p-hydroxybenzylideneaniline had the same infrared spectra.

##### 2. (DA-29-166) Repeat of DA-29-164.

The same quantities of reagents and procedure were used as in DA-29-164, except 10 ml. absolute alcohol was used instead of 7 ml. Evaporation yielded a greenish-yellow semi-solid precipitate which had no distinct melting point. Recrystallization using cold absolute alcohol gave a yellow crystalline material with a greenish tint. As this material was allowed to stand, it turned

pale yellow; it had no definite melting point. The reported melting point is 165-167°C. Its infrared spectra did not yield information from which its structure could be definitely established.

### 3. (DA-29-191) Modification of DA-29-164.

Using the same amounts (0.01 mole each) of benzylidene-p-bromoaniline and p-hydroxybenzylideneaniline as in DA-29-164, the procedure was modified slightly. The p-hydroxy compound was dissolved in 50 ml. of hot, but not boiling, absolute ethanol. Next, benzylidene-p-bromoaniline was added and the reaction mixture cooled immediately in an ice bath. A pale yellow-green substance precipitated from solution; it was separated by filtration and when dried, it was light tan in color. No sharp melting point was found for the compound and during heating it changed color to a bright green. The total amount of substance produced was 1.00 g. The infrared spectra of the green and of the tan materials were identical.

### 4. (DA-29-197) Further Modification of DA-29-164.

p-Hydroxybenzylideneaniline 1.97 g. (0.01 mole) was dissolved in 50 ml. of benzene heated to 60°C. To this solution 2.60 g. (0.01 mole) benzylidene-p-bromoaniline was added. Heating was continued for three minutes, then the reaction was quenched in a dry ice-acetone bath. When the mixture was entirely frozen, the flask was removed from this bath and placed in an ice bath. Then the frozen benzene was sublimed off under reduced pressure leaving 4.40 g. of a product which had no sharp melting point. The infrared spectrum of the product gave evidence only of Schiff base peaks and no peaks attributable to the postulated di-tertiary amine.

### 5. (DA-29-199) Modification of DA-29-164.

Reaction DA-29-164 was modified in the following way. Into a 100 ml. filter flask was placed 0.01 mole p-hydroxybenzylideneaniline. Then 25 ml.

hot absolute ethanol was added, followed by the addition of 0.01 mole of benzylidene-p-bromoaniline. The flask was swirled twice then plunged into a dry ice-acetone bath, whereupon a yellow precipitate crystallized out. The flask was removed to an ice bath and the ethanol evaporated under reduced pressure. A yellow material with a greenish tint was obtained, which melted at 160°C. Infrared spectra gave no further interpretable information. This compound was recrystallized again from cold absolute ethanol and a somewhat more greenish substance was obtained, which also melted at 160°C. A third recrystallization, in the same manner, gave a semi-solid material.

#### 6. (DA-29-193) Reaction of p-Toluidine and Formaldehyde.

Formalin, 12 ml. of 37%, and a solution of 12 g. p-toluidine in 30 cc. absolute ethanol were heated to 45°C and mixed in a beaker with vigorous stirring. The temperature rose rapidly to 60°C; an oil separated which then solidified. The temperature continued rising to 70°C, then the reaction mixture was cooled in an ice bath. The solid product was removed by filtration and recrystallization from absolute ethanol gave a white soluble product and a white insoluble <sup>amorphous</sup> product. The soluble product began to melt at 125°C, and remained cloudy until nearly 200°C, when the melt became clear. No unique bands corresponding to the di-tertiary base appeared in its infrared spectrum.

#### B. Discussion.

Despite the many trials to duplicate the work of Ingold and Piggot, all attempts were unsuccessful. The conditions described by the authors are deceptively simple; however, the correct product, as described by them, could not be obtained. Failure may be due to the extreme instability of the product, or perhaps to some other factor or factors which have not yet been evaluated.

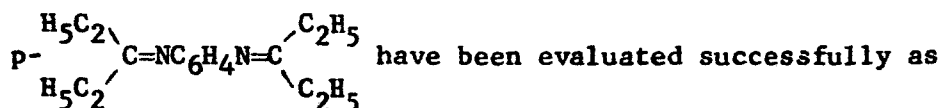
The reaction between p-toluidine and formaldehyde has been reinvesti-

gated<sup>17,18</sup> by Eisner and Wagner and has been found to be far more involved than Ingold reports. The authors of these papers<sup>17,18</sup> report the isolation of no less than six different compounds containing nitrogen from this reaction. Resins have also been shown by these authors to be produced in the reaction. In the light of this newer information, it seems improbable that Ingold actually obtained the diazidines.

## VII. Summary and Conclusions.

1. The data in this report confirm substantially the conclusions of a previous<sup>1</sup> report.
2. The syntheses of a number of monomers reported<sup>1</sup> previously have been repeated, confirming the high-yield data.
3. A number of new monomers having partial or interrupted conjugation have been prepared for use in polymer syntheses for comparison with monomers having uninterrupted conjugation.

4. Two ketanil-type monomers,  $p\text{-}\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{NC}_6\text{H}_4\text{N}=\text{C} \\ \diagup \\ \text{C}_3\text{H}_7 \end{array}$  and



have been evaluated successfully as reagents in Schiff base exchange reactions both in monomeric and polymeric systems. The ketone is displaced readily in these reactions by monofunctional and difunctional aromatic aldehydes.

5. Black polymers are readily obtained in Schiff base reactions when ketanil-type monomers are used as one of the reactants. Polymer yields are high due probably to the side reactions of the liberated ketone or ketone derivative.
6. The polymers prepared from aromatic dialdehydes and diamines by regular solution methods<sup>1</sup> are brick-dust, yellow, and infusible. When the polymerization is performed in certain solvents, such as DMF and DMA, low molecular weight insoluble polymers are also obtained, but they can be melted and carried to high molecular weight dark polymers.
7. Molten benzalaniline is the most active medium in which to perform the polymerization. It appears to function not only



as a solvent but also as a telomerizing agent, thereby accounting for higher-than-theoretical yields calculated on the basis that benzalaniline is only a solvent and not a reagent.

8. No evidence could be found in extensive studies using IR techniques for the existence of four-membered ring complexes or adducts in the polymer. Solvated benzalaniline could be removed from the polymer by continuous extraction in an amount that corresponds approximately to the amount that is removed readily by heating the polymer to about 300-350°C. This indicates that the unrecovered amount exists as telomers in the polymer which could be eliminated by chain-end reactions on continued heating.
9. Attempts to confirm the existence of four-membered ring adducts<sup>14,15</sup> using non-polymerizing systems were unfruitful.
10. The high melt- or "solid-" viscosity of the polymer requires prolonged heating at about 400°C to permit chain-end coupling to occur and thereby to eliminate telomerized benzalaniline. In such a medium, the removal appears to be diffusion-controlled. Low pressures of the order of 0.5 mm Hg pressure or lower are beneficial. In those syntheses of polymer where the eliminated product is of a lower molecular weight or of a higher vapor pressure than benzalaniline, as for example,  $C_2H_5OH$ ,  $C_3H_7OH$  and  $C_6H_5CH(OC_2H_5)_2$ , diffusion of the by-product occurs more readily and the theoretical yields are more easily approached.
11. Both monomeric and polymeric Schiff bases appear to be very thermally stable compounds.
12. High molecular weight benzalaniline-telomerized polymeric Schiff

bases also appear to be thermally stable, as evidenced by the higher-than-theoretical yield when heated for extended periods at 360-420°C, the nature and small amount of distillate recovered during such heating and from little or no change in the IR spectra of the polymers.

13. Meta-phenylenediamine or its selected derivatives appears to be a better reactant than para-phenylenediamine in the synthesis of the polymer permitting a longer fusible stage than the para compounds. This is attributed to the configuration of the polymer. No final conclusion can be drawn at this time to the relative thermal stabilities of the meta- and para-polymers, though both appear to be high. Differential thermal analyses will be performed to resolve this point when the DTA apparatus, which has been ordered, is received.
14. Modifications of the polymerization reaction of the xylylidene-tetraalkyl ethers with aromatic amines or their derivatives appear to be promising with almost theoretical yields and black polymers in a number of cases.
15. Post-heating of non-black polymeric Schiff bases in benzal-aniline converts them to black polymers.
16. Attempts to solubilize black polymeric Schiff bases by preparing acyl derivatives were not successful. The absence of true solvents for these polymers makes molecular weight determination by the currently accepted methods impossible.

### VIII. Future Studies.

Sufficient significant data has been acquired from the preliminary studies to allow the selection of the most suitable systems for the next phase of the research on this project.

Particular attention and effort will be given to the kinetics of the reactions and to the evaluation of the polymers by means of differential thermal analysis.

The investigations will be divided into two parts:

- A) The Polymeric Schiff Bases;
- B) The Polymeric Azines.

These two classes are fundamentally different. The polymeric Schiff bases can be considered as polymers which possess the requirements essential to thermal stability. In contrast, the polymeric azines,  $\left[ \text{HCArCH=N-N} \right]_n$ , are less stable but have relatively high decomposition temperatures. In the process of decomposition, it appears that the polyazines become converted to the more thermally stable polystilbene-type polymers, and thus appear to offer promise as carbonizing ablators. The absence of literature references on the behavior of this or related polymers will require studies on prototype non-polymeric azines.

The systems to be studied during the next phase of this research are:

#### A) Polymeric Schiff Bases

##### 1) Bis-Exchange Reactions

- a) Bis-exchange of  $p\text{-C}_6\text{H}_5\text{CH=NC}_6\text{H}_4\text{N=CHC}_6\text{H}_5$  with  $p\text{-C}_6\text{H}_5\text{N=CHC}_6\text{H}_4\text{CH=NC}_6\text{H}_5$ .
- b) Bis-exchange of  $m\text{-C}_6\text{H}_5\text{CH=NC}_6\text{H}_4\text{N=CHC}_6\text{H}_5$  with  $p\text{-C}_6\text{H}_5\text{N=CHC}_6\text{H}_4\text{CH=NC}_6\text{H}_5$
- c) Bis-exchange of Al<sup>a</sup>) in  $\text{C}_6\text{H}_5\text{CH=NC}_6\text{H}_5$

d) Bis-exchange of Alb) in  $C_6H_5CH=NC_6H_5$

## 2) Aldehyde Condensation Reactions

a)  $p-C_6H_4(CHO)_2$  with  $p-C_6H_4(NH_2)_2$  in  $C_6H_5CH=NC_6H_5$

b)  $p-C_6H_4(CHO)_2$  with  $m-C_6H_4(NH_2)_2$  in  $C_6H_5CH=NC_6H_5$

c) Prepolymer of  $p-C_6H_4(CHO)_2$  with  $p-C_6H_4(NH_2)_2$  in  $C_6H_5CH=NC_6H_5$

d) Prepolymer of  $p-C_6H_4(CHO)_2$  with  $m-C_6H_4(NH_2)_2$  in  $C_6H_5CH=NC_6H_5$

## 3) Acetal Reactions

a)  $C_6H_4[CH(OR)_2]_2$  with  $m-C_6H_4(NH_2)_2$

b)  $C_6H_4[CH(OR)_2]_2$  with  $m-C_6H_4(NH_2)_2$  in  $C_6H_5N=CHC_6H_5$

c)  $C_6H_4[CH(OR)_2]_2$  with  $m-C_6H_4(N=CHC_6H_5)_2$

d)  $C_6H_4[CH(OR)_2]_2$  with  $m-C_6H_4(N=CHC_6H_5)_2$  in  $C_6H_5N=CHC_6H_5$

## 4) Polymers with Interrupted Conjugation

### a) Polymers Based on Monomers

i)  $C_6H_5-CH=N-C_6H_4-CH_2-C_6H_4-N=CH-C_6H_5$

ii)  $C_6H_5-CH=N-(CH_2)_4-N=CH-C_6H_5$

iii)  $C_6H_5-CH=N-(CH_2)_6-N=CH-C_6H_5$

iv)  $C_6H_5-CH=N-C_6H_4-O-C_6H_4-N=CH-C_6H_5$

v)  $C_6H_5-CH=N-C_6H_4-NH-C_6H_4-N=CHC_6H_5$

## B) Polymeric Azines

### 1) Prototype Compounds

a) Syntheses of  $XC_6H_4CH=N-N=CHC_6H_4Y$  compounds

b) Decomposition studies on  $XC_6H_4CH=N-N=CHC_6H_4Y$  compounds

### 2) Polymers

a) Syntheses of  $\{CHC_6H_4CH=N-N\}_n$

i) By aldehyde and amine reactions

ii) By exchange method reactions

b) Decomposition studies of  $\{HCC_6H_4CH=N-N\}_n$

IX. Acknowledgment.

The authors and the University of Notre Dame acknowledge gratefully the financial assistance from NASA which made this research possible. Appreciated also is the general guidance and assistance given by Mr. Bernard Achhammer, NASA Headquarters, Washington, D. C.

X. Glossary.

BA	=	$\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$
PPDA	=	$\text{p-H}_2\text{NC}_6\text{H}_4\text{NH}_2$
TA	=	$\text{p-OHCC}_6\text{H}_4\text{CHO}$
DBPPDA	=	$\text{p-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$
PXDA	=	$\text{p-C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$
D-2-PPFDA	=	$\text{p-} \begin{array}{c} \text{H}_7\text{C}_3 \backslash \\ \text{C}=\text{NC}_6\text{H}_4\text{N}=\text{C} \begin{array}{l} \text{C}_3\text{H}_7 \\ \text{C}_2\text{H}_5 \end{array} \\ \text{H}_5\text{C}_2 / \end{array}$
D-3-PPFDA	=	$\text{p-} \begin{array}{c} \text{H}_5\text{C}_2 \backslash \\ \text{C}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{C} \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \\ \text{H}_5\text{C}_2 / \end{array}$
BDE	=	$\text{C}_6\text{H}_5\text{CH}(\text{OC}_2\text{H}_5)_2$
XTE	=	$\text{p-} \begin{array}{c} \text{H}_5\text{C}_2\text{O} \backslash \\ \text{CH}-\text{C}_6\text{H}_4-\text{CH} \begin{array}{l} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{array} \\ \text{H}_5\text{C}_2\text{O} / \end{array}$
MPDA	=	$\text{m-H}_2\text{NC}_6\text{H}_4\text{NH}_2$
DBMPD	=	$\text{m-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$
XTBE	=	$\text{p-} \begin{array}{c} \text{H}_9\text{C}_4\text{O} \backslash \\ \text{HC}-\text{C}_6\text{H}_4-\text{CH} \begin{array}{l} \text{OC}_4\text{H}_9 \\ \text{OC}_4\text{H}_9 \end{array} \\ \text{H}_9\text{C}_4\text{O} / \end{array}$
DMA	=	$\text{CH}_3\text{CON}(\text{CH}_3)_2$
DMF	=	$\text{HCON}(\text{CH}_3)_2$
DAPD	=	$\text{p-CH}_3\text{CONHC}_6\text{H}_4\text{NHOCCH}_3$
MBPD	=	$\text{p-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{NH}_2$

## XI. Bibliography.

1. G.F. D'Alelio, L. Mallavarapu, T. Huemmer, T. Kurosaki, W. Fessler and J. Crivello, "Fundamental Studies on the Synthesis of Heat-Resistant Polymers." Report Number 4 to NASA, September 1964.
2. A.I. Vogel, "A Textbook of Practical Organic Chemistry," Green and Company, London, New York and Toronto, 1946.
3. L.A. Bigelow, H. Eatough, Organic Syntheses, Collective Volume I, John Wiley and Sons, Second Edition, 1941.
4. G. Reddelien, H. Danilof, Ber., 54, 3138 (1921).
5. O. Fischer, Ber., 14, 2525 (1881).
6. M. Lazorenko, Jahrber. Fortschr. Chem., 760 (1870).
7. H. Hertzfeld, Ber., 10, 1271 (1877).
8. W. Miller, J. Plöchl, Ber., 25, 2053 (1893).
9. G. Sunagawa, Pharm. Bull. (Japan), 3, 109 (1955).
10. J.L. Szuko and W.A. Bruce, U.S.P. 2,739,981, March 22, 1956.
11. W.R. Boon and A.R. Lowe, U.S.P. 2,387,873, October 30, 1945.
12. G. Reddelien, Ber., 54B, 3121 (1921).
13. B.E. Davydov, B.A. Kuntzel, U.A. Papov, and W.V. Prokofyeva, "High Molecular Compounds," USSR, Volume II, No. 3, 321 (1963).
14. C.K. Ingold and H.A. Piggot, J. Chem. Soc., 121, Part 2, 2793 (1922).
15. C.K. Ingold and H.A. Piggot, J. Chem. Soc., 123, 2745 (1923).
16. G.M. Badger, C.P. Joshua and G.E. Lewis, Tetrahedron Letters, 3711 (1964).
17. A. Eisner, E.C. Wagner, J. Am. Chem. Soc., 56, 138 (1934).
18. E.C. Wagner, J. Am. Chem. Soc., 56, 1944 (1934).
19. R. Alquier, Bull. Soc. Chem. 10, 197 (1943).